Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Aluminium alkyl complexes with imidazolin-2-phosphanamidinate ligand as precursor for catalytic guanylation reactions of carbodiimides

Contents

TS1. Crystallographic data and refinement parameters of 1b and 1c.

Crystal parameters	**1b**	**1c**
CCDC NO.	2124041	2124043
Empirical formula	$C_{39}H_{47}N_4P$	$C_{29}H_{43}N_4P$
Formula weight	602.81	478.66
T (K)	249.99(10)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	9.4611(2)	10.4218(5)
b (Å)	12.4141(3)	14.9253(7)
c (Å)	16.7883(4)	20.5378(9)
α (°)	101.570(2)	90
β (°)	100.081(2)	100.693(5)
γ (°)	111.127(2)	90
V (Å^3)	1734.64(7)	3139.2(3)
Z	2	16
D_{calc} (g cm^{-3})	1.158	1.072
μ (mm^{-1})	0.112	0.111
F(000)	652	1104
Theta range for data collection	2.617 to 28.908 deg.	2.9100 to 26.3390 deg.
Limiting indices	-12 <= h <= 12, -16 <= k <=16, -20 <=l <= 22	-13<=h<=13, -18<=k<=20, -22<=l<=27
Reflections collected / unique	27111 / 8000 [R(int) = 0.0378]	28830 / 7361 [R(int) = 0.0552]
Completeness of theta	99.80 %	99.64 %
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.76682	1.00000 and 0.71528
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8000 / 0 / 410	7361 / 0 / 338
Goodness-of-fit on F^2	1.084	1.045
Final R indices [I>2Sigma(I)]	R1 = 0.0461,	R1 = 0.0899,

	wR2 = 0.1275	wR2 = 0.2664
R indices (all data)	R1 = 0.0571, wR2 = 0.1344	R1 = 0.1174, wR2 = 0.2856

TS1. (contd). Crystallographic data and refinement parameters of 2a, 2b and 2c.

Crystal parameters	**2a**	**2b**	**2c**
CCDC NO.	2124040	2124042	2124039
Empirical formula	$C_{47}H_{64}N_4PAl$	$C_{41}H_{52}N_4PAl$	$C_{31}H_{48}N_4Pal$
Formula weight	743.01	658.85	534.71
T (K)	298	250(10)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	13.5229(5)	10.2350(2)	15.5979(6)
b (Å)	18.5921(8)	19.8700(3)	10.9206(4)
c (Å)	18.0626(8)	20.5541(4)	18.8109(6)
α (°)	90	99.080(2)	90
β (°)	100.669(4)	91.255(2)	100.611(3)
γ (°)	90	100.416(2)	90
V (Å^3)	4462.8(3)	4054.20(13)	3149.4(2)
Z	4	2	4
D_{calc} (g cm^{-3})	1.104	1.111	1.128
μ (mm^{-1})	0.116	0.122	0.140
F(000)	1604	1458	1160
Theta range for data collection	3.0270 to 27.7710 deg.	2.641 to 29.080	3.2390 to 26.8690 deg.
Limiting indices	-14<=h<=18, -23<=k<=25, -24<=l<=18	-13<=h <=12, -24 <= k <=26, -27 <= l <= 27	-20<=h<=19, -14<=k<=14, -24<=l<=21
Reflections collected / unique	39839 / 10308 [R(int) = 0.0744]	89802 / 19084 [R(int) = 0.0314]	25063 / 7205 [R(int) = 0.0402]
Completeness of theta	99.71 %	99.80 %	99.13 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan

Max. and min. transmission	1.00000 and 0.95218	1.00000 and 0.88174	1.00000 and 0.82770
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10308 / 24 / 497	19084 / 0 /898	7205 / 0 / 346
Goodness-of-fit on F^2	1.051	1.050	1.055
Final R indices [I>2Sigma(I)]	R1 = 0.0682, wR2 = 0.1888	R1 = 0.0424, wR2 = 0.1150	R1 = 0.0432, wR2 = 0.1189
R indices (all data)	R1 = 0.0916, wR2 = 0.2038	R1 = 0.0579, wR2 = 0.1224	R1 = 0.0583, wR2 = 0.1271

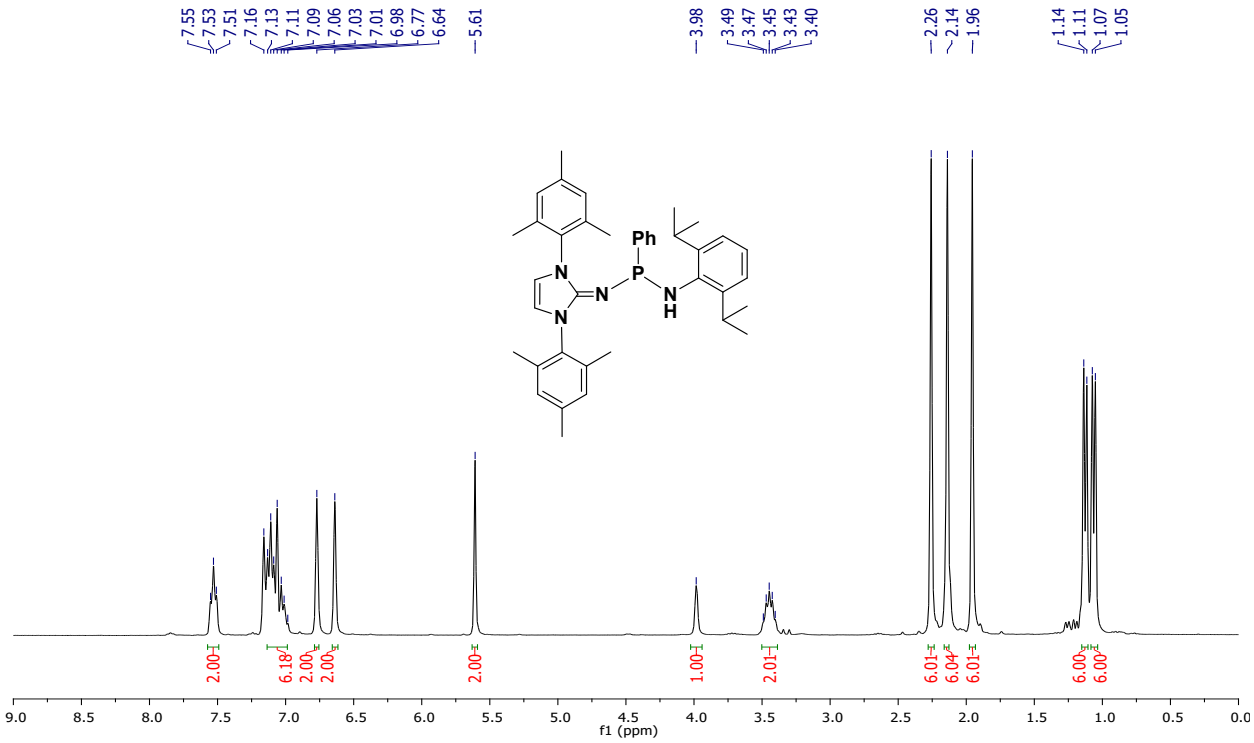


Figure FS1. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of **1b**.

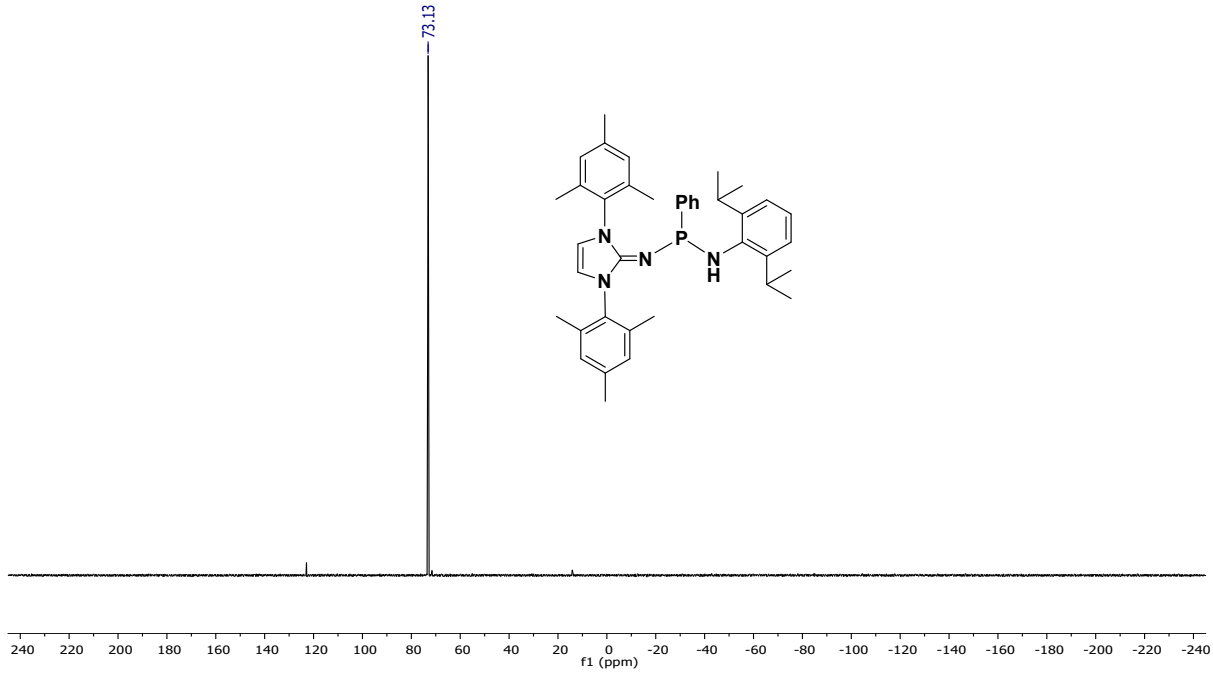


Figure FS2. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 25 °C C_6D_6) spectrum of **1b**.

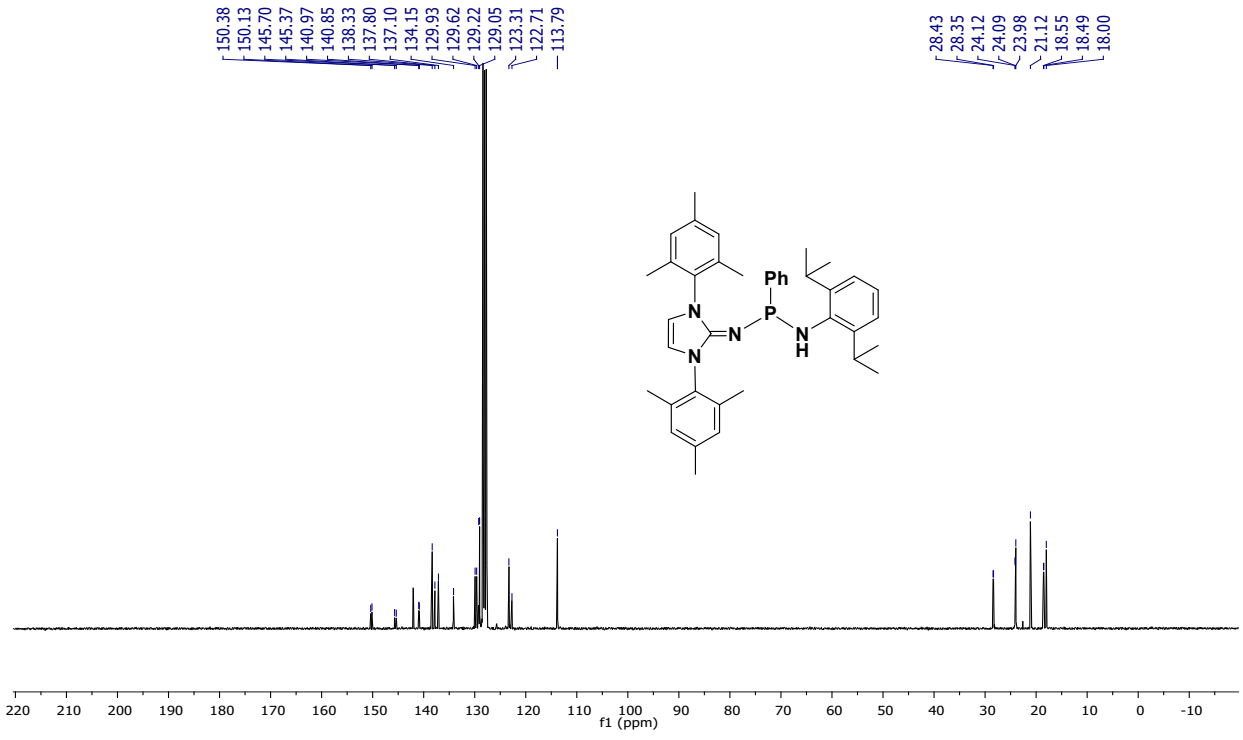


Figure FS3. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, C_6D_6) spectrum of **1b**.

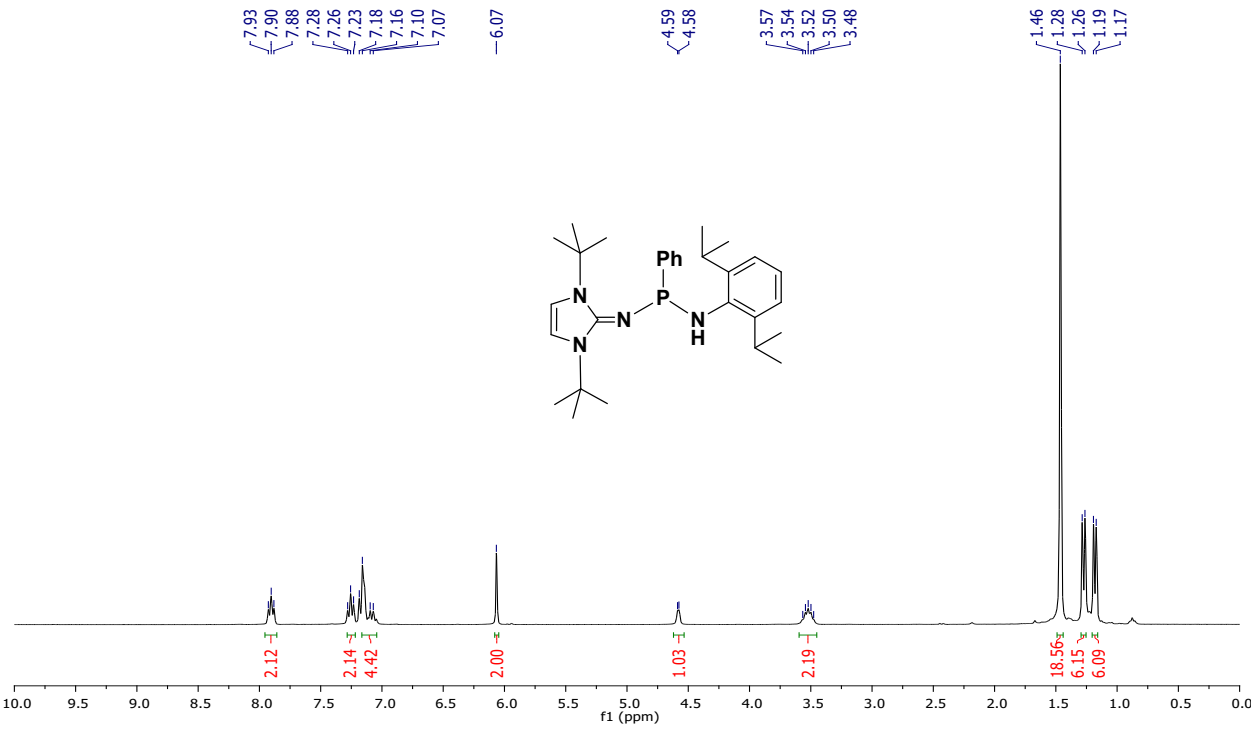


Figure FS4. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of **1c**.

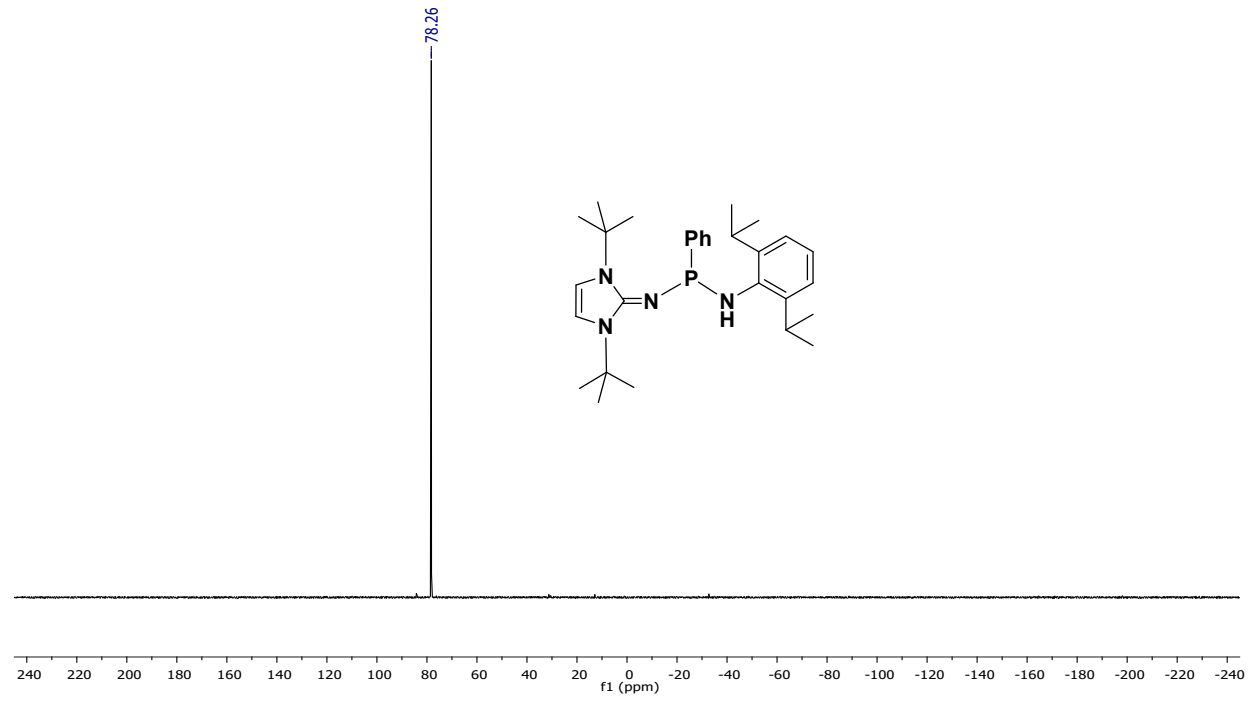


Figure FS5. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 25 °C, C_6D_6) spectrum of **1c**.

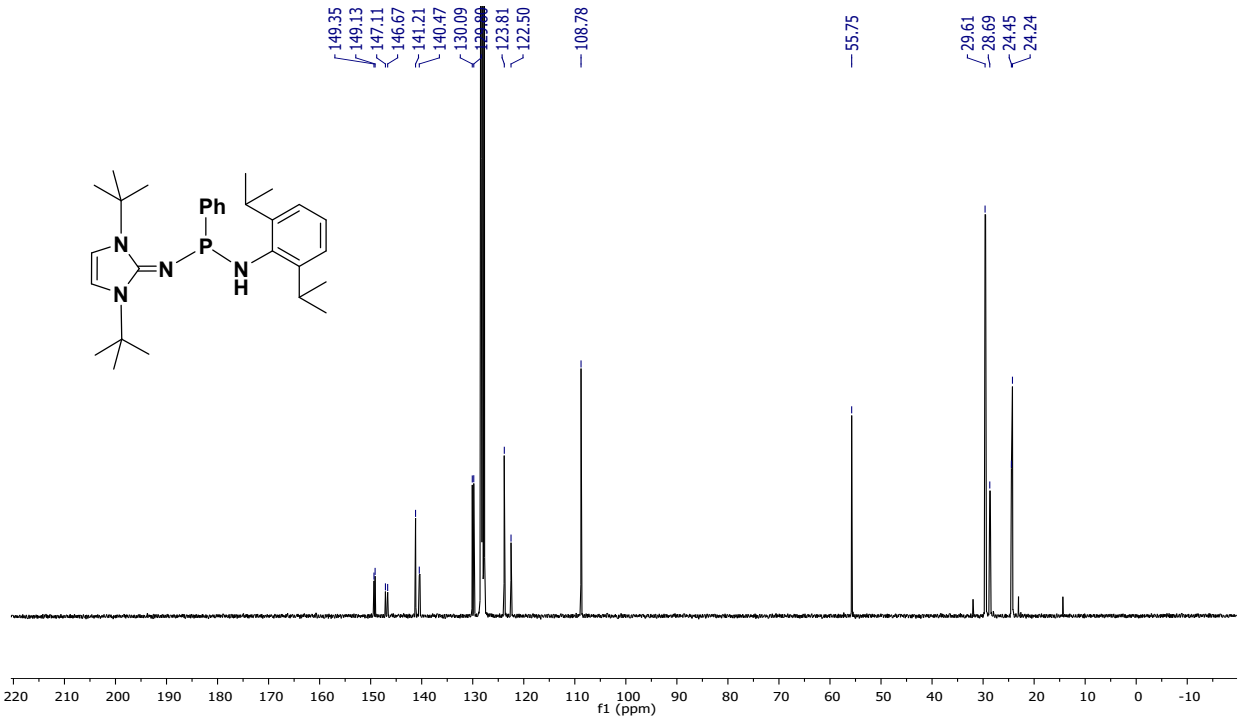


Figure FS6. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, C_6D_6) spectrum of **1c**.

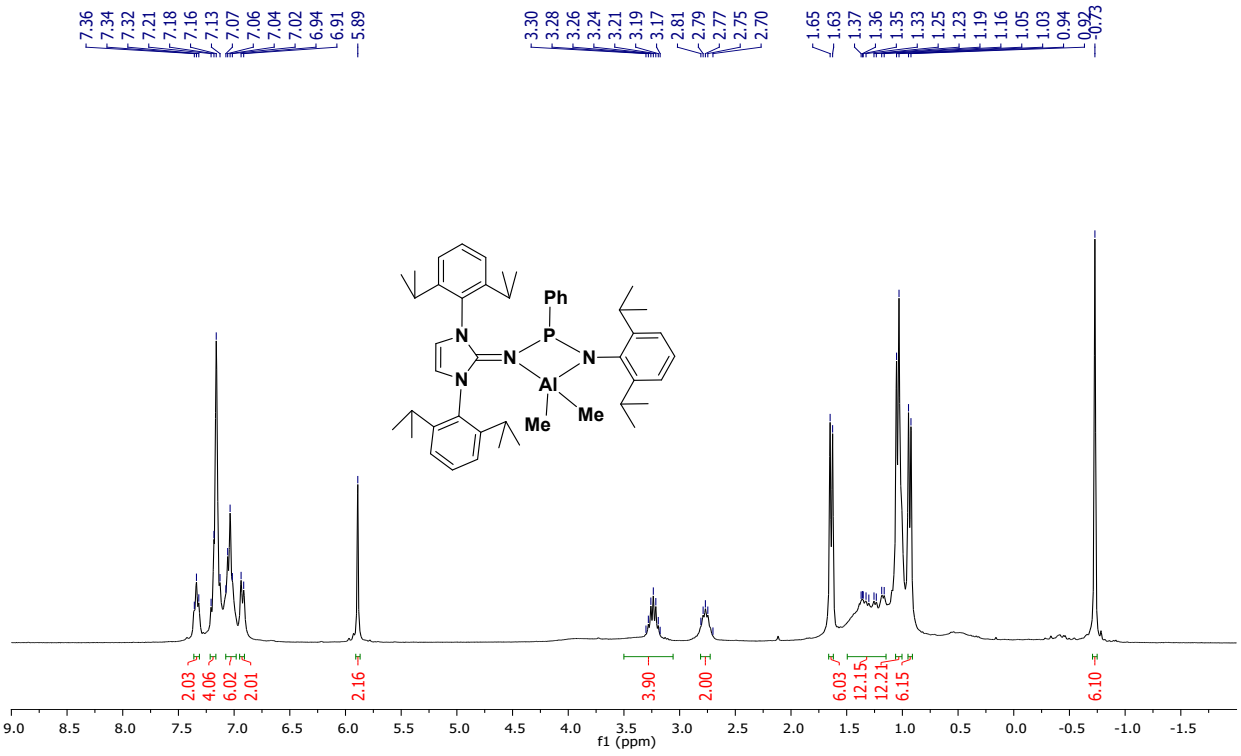


Figure FS7. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of **2a**.

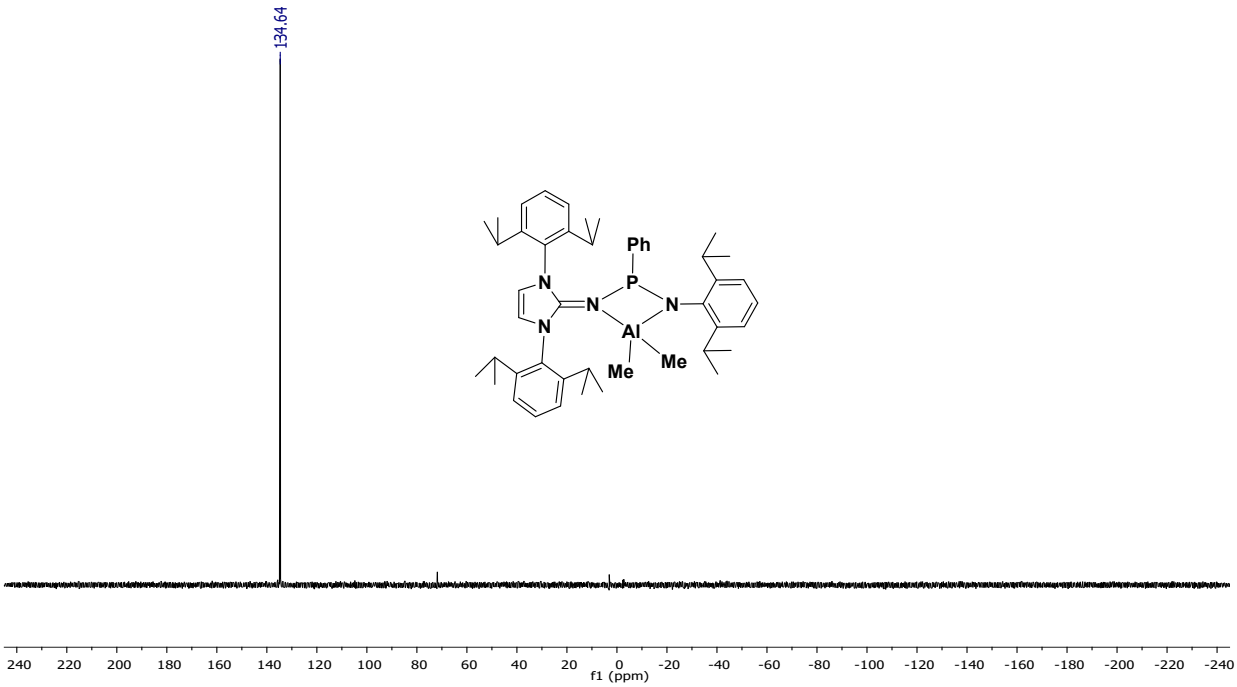


Figure FS8. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 25 °C, C_6D_6) spectrum of **2a**.

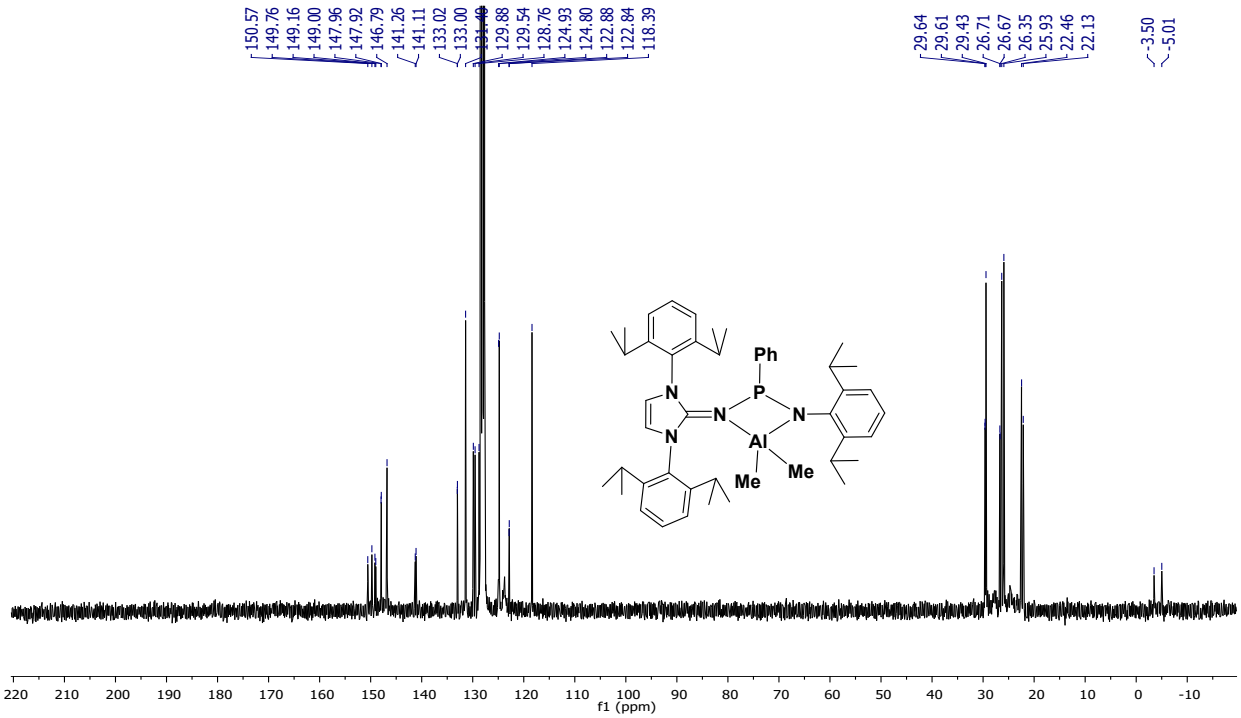


Figure FS9. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, C_6D_6) spectrum of **2a**.

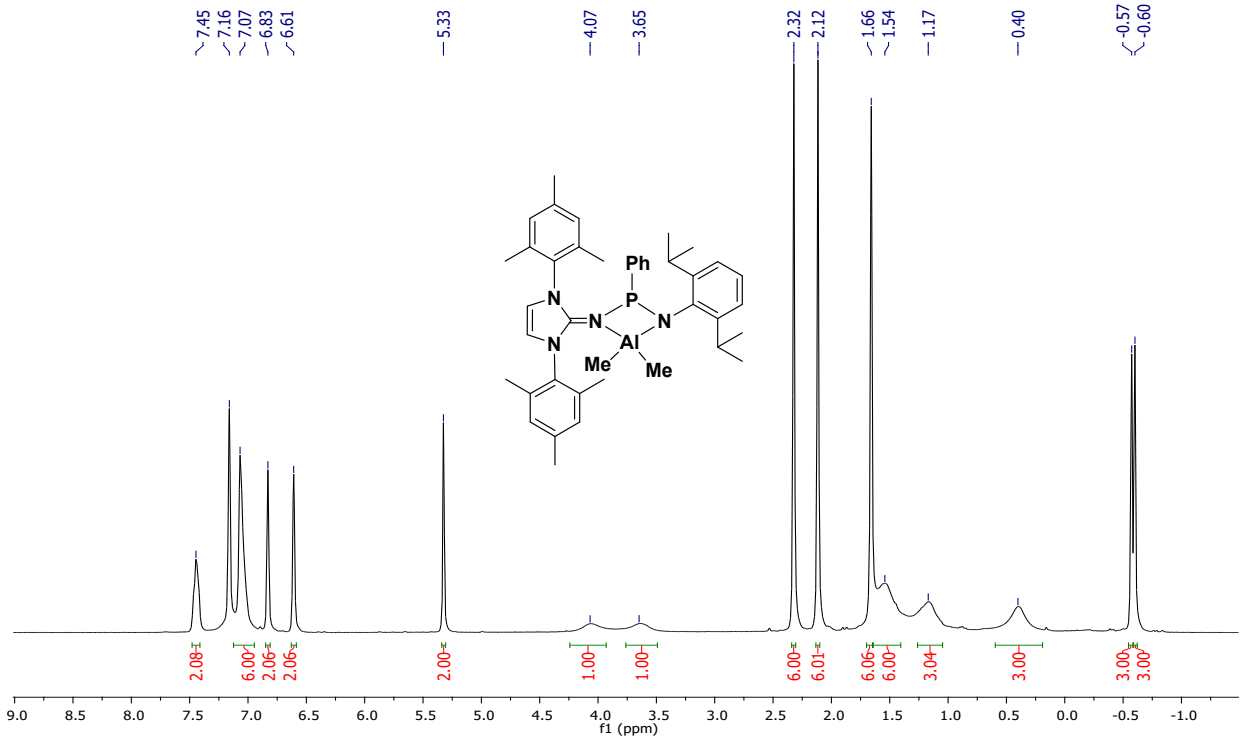


Figure FS10. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of **2b**.

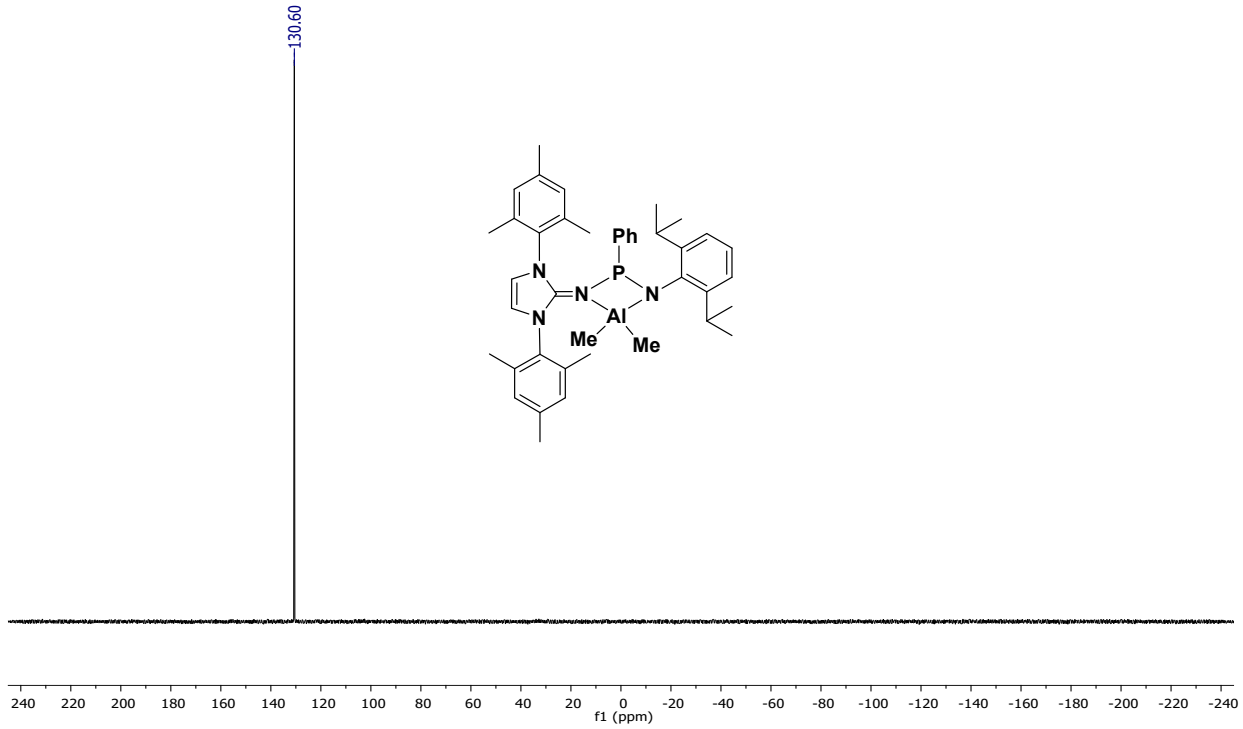


Figure FS11. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 25 °C, C_6D_6) spectrum of **2b**.

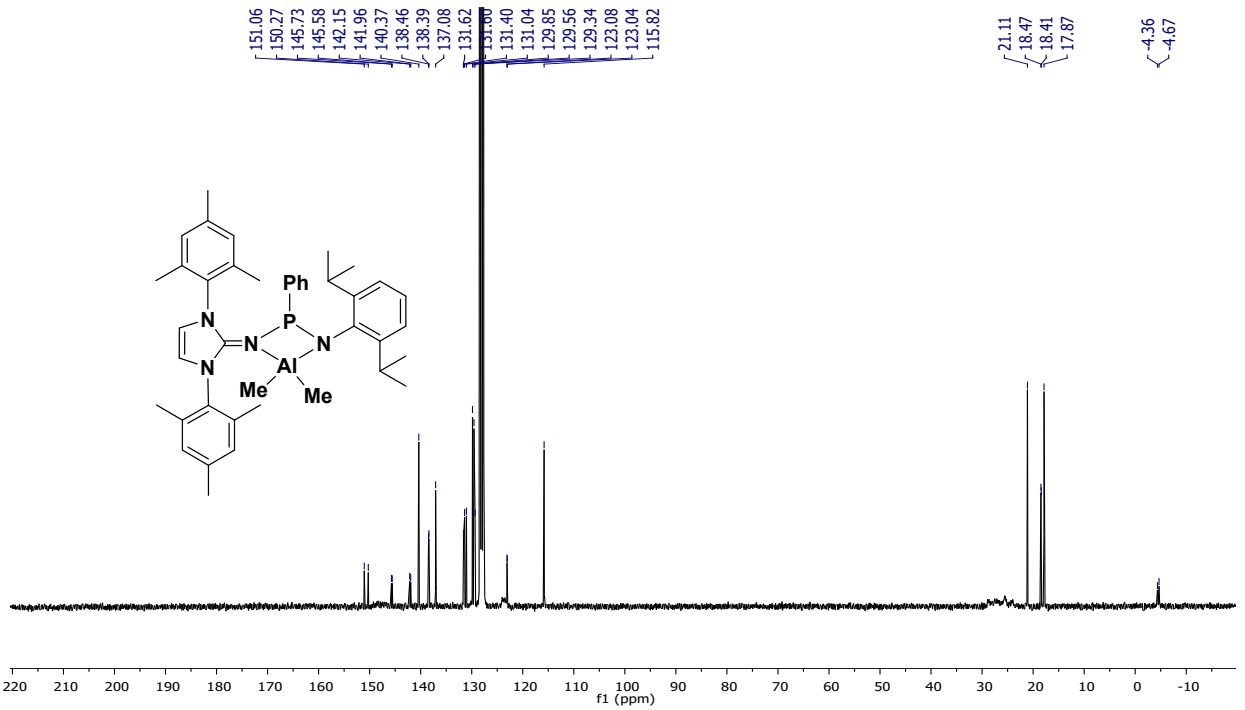


Figure FS12. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, C_6D_6) spectrum of **2b**.

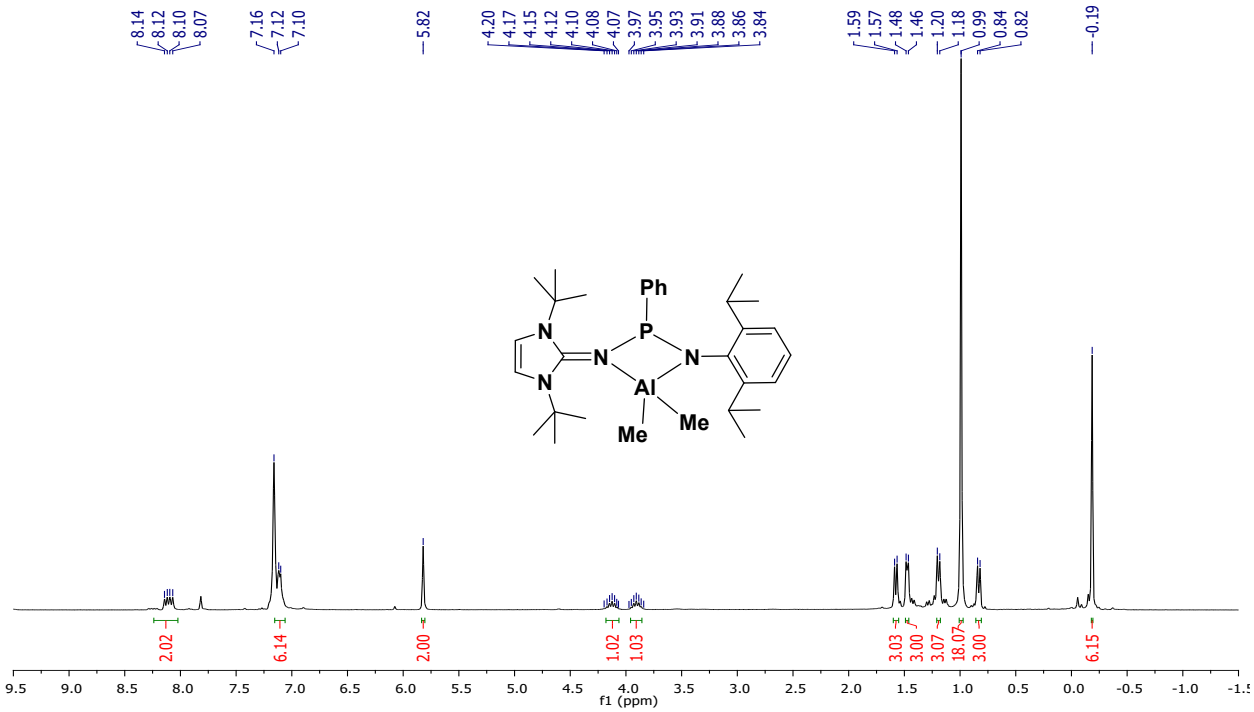


Figure FS13. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of **2c**.

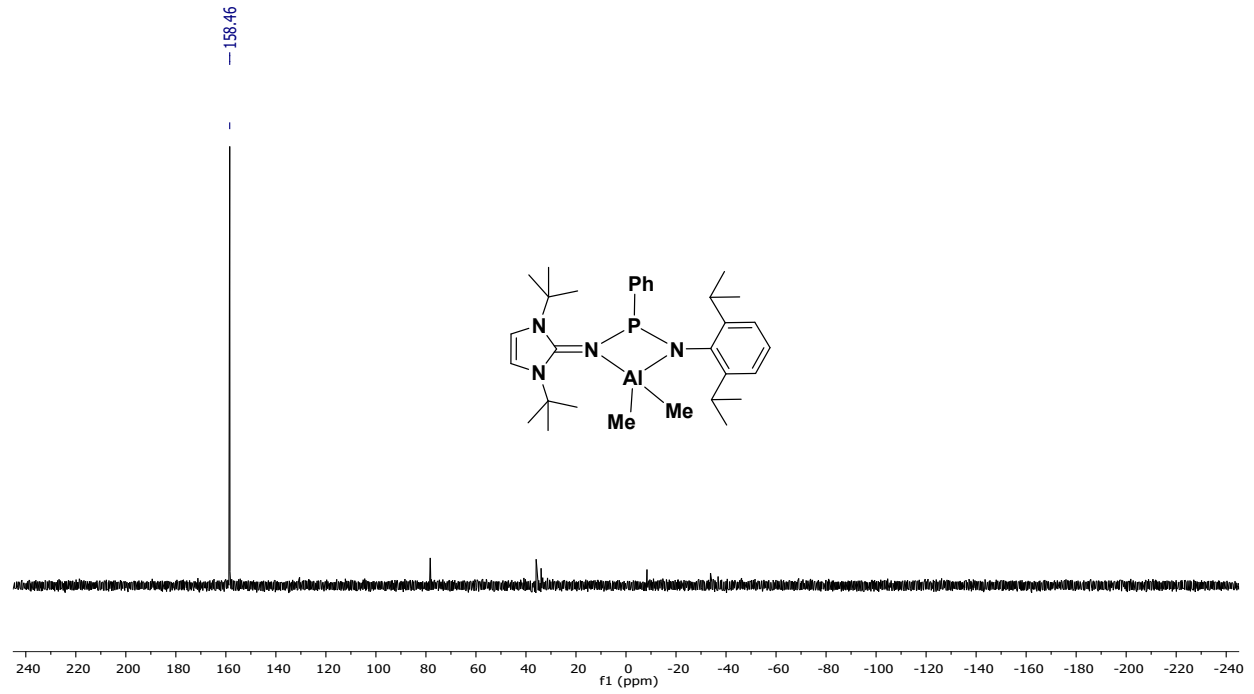


Figure FS14. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 25 °C, C_6D_6) spectrum of **2c**.

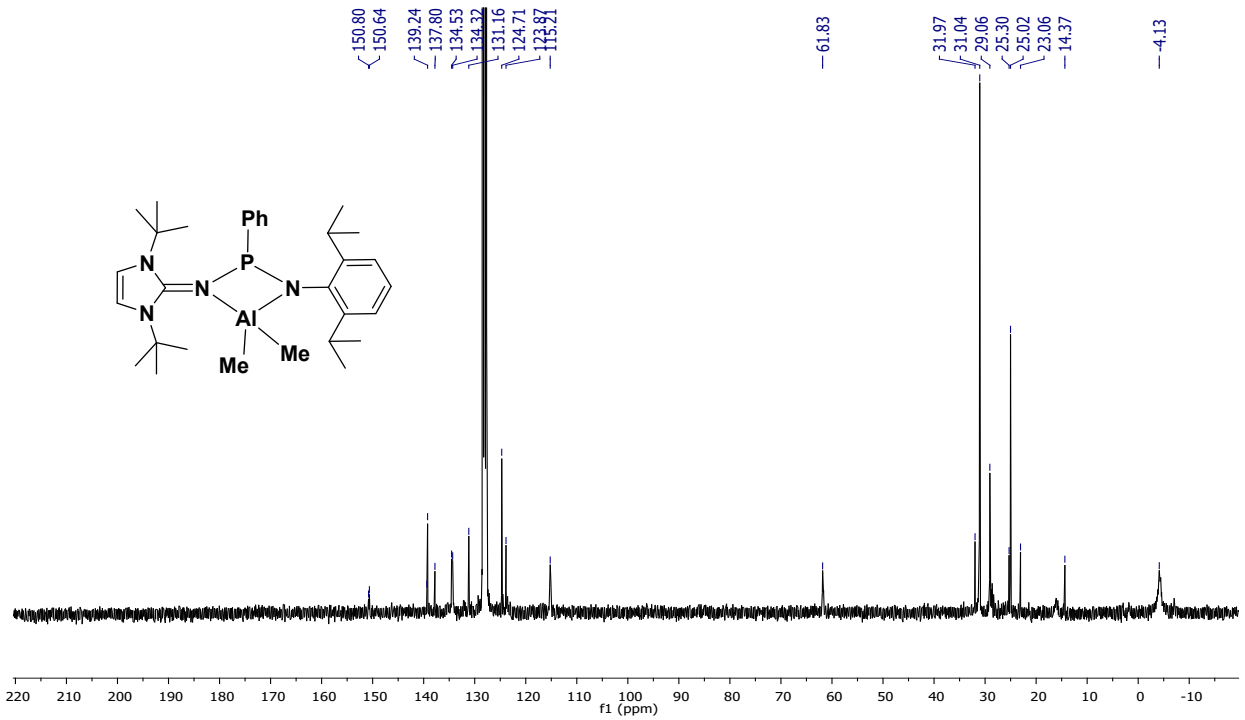
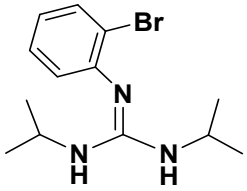


Figure FS15. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, C_6D_6) spectrum of **2c**.

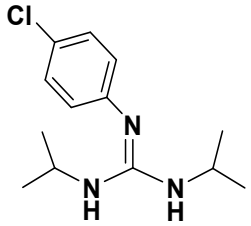
NMR data of guanidine products:

***N*-(2-bromophenyl)-*N'*, *N"*-diisopropylguanidine (3a)**



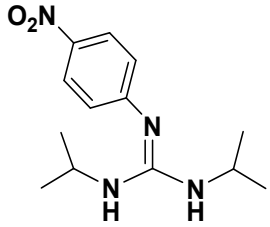
Yield: 88%. ^{1}H-NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.53 (d, J = 9.0 Hz, 1H), 7.20 - 7.15 (m, 1H), 6.89 (d, J = 6.0 Hz, 1H), 6.82 - 6.77 (m, 1H), 3.81 - 3.73 (m, 2H), 3.46 (br, 2H), 1.18 (d, J = 6.0 Hz, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 149.78, 148.55, 133.12, 128.28, 125.06, 122.83, 119.49, 43.42, 23.57 ppm. The NMR data are in accordance with the literature.[1]

***N*-(4-chlorophenyl)-*N'*, *N"*-diisopropylguanidine (3b)**



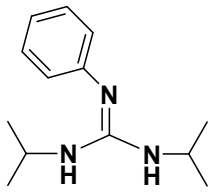
Yield: 84%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.19 (d, J = 6.0 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 3.76 - 3.72 (m, 2H), 3.53 (br, 2H), 1.16 (d, J = 6.0 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.32, 149.17, 129.32, 126.32, 124.92, 43.33, 23.42 ppm. The NMR data are in accordance with the literature.[2]

***N*-(4-nitrophenyl)-*N'*, *N"*-diisopropylguanidine (3c)**



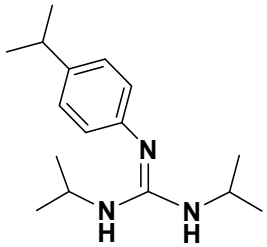
Yield: 78%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 8.09 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 3.81 (br, 4H), 1.19 (d, J = 6.0 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 158.45, 150.58, 141.06, 125.72, 122.92, 43.56, 23.36 ppm. The NMR data are in accordance with the literature.[2]

***N*-phenyl-*N'*, *N"*-diisopropylguanidine (3d)**



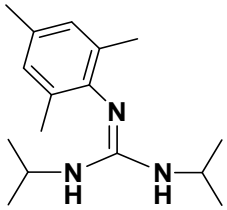
Yield: 83%. ^{1}H-NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.26 - 7.22 (m, 2H), 6.95 - 6.90 (m, 1H), 6.87 - 6.84 (m, 2H), 3.81 - 3.73 (m, 2H), 3.56 (br, 2H), 1.16 (d, J = 6.0 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.43, 150.24, 129.36, 123.66, 121.45, 43.32, 23.47 ppm. The NMR data are in accordance with the literature.[2]

***N*-(4-isopropylphenyl)-*N'*, *N"*-diisopropylguanidine (3e)**



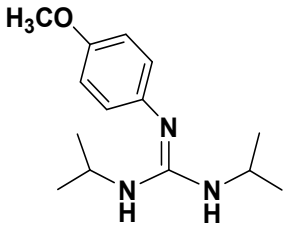
Yield: 82%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.09 (d, J = 9.0 Hz, 2H), 6.76 (d, J = 6.0 Hz, 2H), 3.79 - 3.71 (m, 2H), 2.88 - 2.79 (m, 1H), 1.22 (d, J = 9.0 Hz, 6H), 1.14 (d, J = 6.0 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.22, 147.72, 141.57, 127.14, 123.13, 43.21, 33.43, 24.21, 23.37 ppm. The NMR data are in accordance with the literature.[2]

***N*-(2,4,6-trimethylphenyl)-*N'*, *N"*-diisopropylguanidine (3f)**



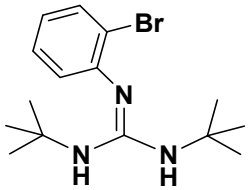
Yield: 75%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 6.79 (s, 2H), 4.09 (bs, 2H), 3.36 (br, 2H), 2.22 (s, 3H), 2.06 (s, 6H), 1.14 (br, 12H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 148, 143.62, 130.65, 130.53, 128.62, 43.10, 23.64, 20.80, 18.19 ppm. The NMR data are in accordance with the literature.[3]

***N*-(4-methoxyphenyl)-*N'*, *N"*-diisopropylguanidine (3g)**



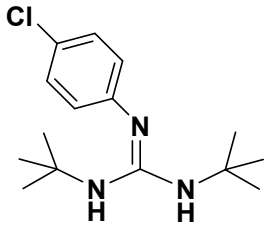
Yield: 88%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 6.82 - 6.74 (m, 4H), 3.76 (s, 3H), 3.52 (br, 2H), 1.14 (d, J = 6.0 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 154.58, 150.72, 143.34, 124.27, 114.66, 55.47, 43.24, 23.43 ppm. The NMR data are in accordance with the literature.[4]

***N*-(2-bromophenyl)-*N'*, *N"*-ditertbutylguanidine (3h)**



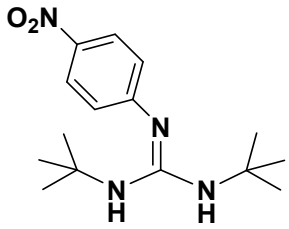
Yield: 83%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.54 - 7.52 (m, 1H), 7.20 - 7.14 (m, 1H), 6.83 - 6.74 (m, 2H), 3.62 (br, 2H), 1.36 (s, 18H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 149.72, 148.43, 133.17, 128.19, 124.31, 122.50, 119.24, 51.02, 30.27 ppm.

***N*-(4-chlorophenyl)-*N'*, *N"*-ditertbutylguanidine (3i)**



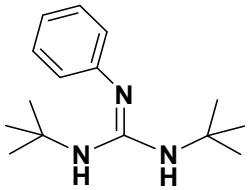
Yield: 85%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.21 (d, J = 9.0 Hz, 2H), 6.74 (d, J = 9.0 Hz, 2H), 3.69 (br, 2H), 1.35 (s, 18H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.34, 149.45, 129.26, 126.09, 124.43, 50.92, 30.18 ppm. The NMR data are in accordance with the literature.[5]

***N*-(4-nitrophenyl)-*N'*, *N"*-ditertbutylguanidine (3j)**



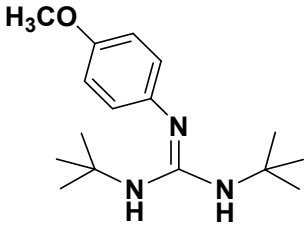
Yield: 75%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 8.06 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.43 (br, 2H), 1.27 (s, 18H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 152.69, 126.48, 113.47, 55.05, 31.44 ppm.

_N_-phenyl-_N'_, _N"_-ditertbutylguanidine (3k)



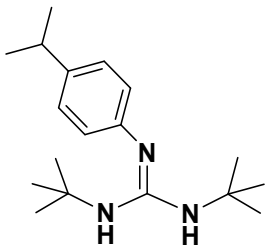
Yield: 81%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.16 - 7.11 (m, 2H), 6.82 - 6.77 (m, 1H), 6.70 - 6.67 (m, 2H), 3.57 (br, 2H), 1.23 (s, 18H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.79, 150.16, 129.31, 123.18, 121.22, 50.87, 50.78, 30.19 ppm. The NMR data are in accordance with the literature.[5]

_N_-(4-methoxyphenyl)-_N'_, _N"_-ditertbutylguanidine (3l)



Yield: 83%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 6.81 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H), 3.66 (br, 2H), 1.32 (s, 18H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 154.47, 150.73, 143.96, 123.79, 114.70, 55.57, 50.80, 30.18 ppm.

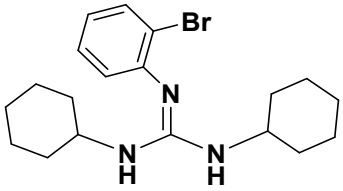
_N_-(4-isopropylphenyl)-_N'_, _N"_-ditertbutylguanidine (3m)



Yield: 81%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.11 (d, J = 6.0 Hz, 2H), 6.73 (d, J = 6.0 Hz, 2H), 3.71 (br, 2H), 2.90 - 2.81 (m, 1H), 1.35 (s, 18H), 1.24 (d, J = 6.0 Hz, 6H) ppm. ^{13}C{^{1}H} NMR

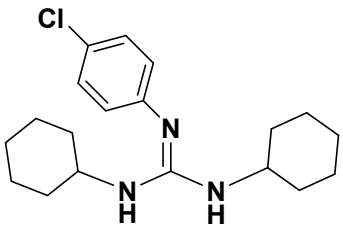
(75 MHz, 25 °C, $CDCl_3$): δ_c 150.18, 148.23, 141.48, 127.18, 122.77, 115.28, 50.81, 33.54, 30.19, 24.32 ppm.

_N_-(2-bromophenyl)-_N'_, _N"_-dicyclohexylguanidine (3n)



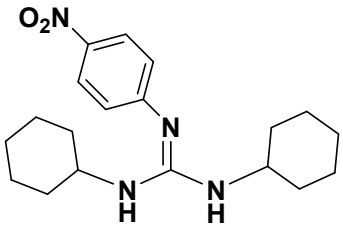
Yield: 85%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.53 (d, J = 9.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 6.0 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 3.42 (br, 2H), 2.04 (d, J = 12 Hz, 4H), 1.71 - 1.57 (m, 6H), 1.41 - 1.29 (m, 4H), 1.20 - 1.05 (m, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 149.69, 148.69, 133.16, 128.30, 125.20, 122.85, 119.65, 50.31, 34.00, 25.80, 25.03 ppm. The NMR data are in accordance with the literature.[2]

_N_-(4-chlorophenyl)-_N'_, _N"_-dicyclohexylguanidine (3o)



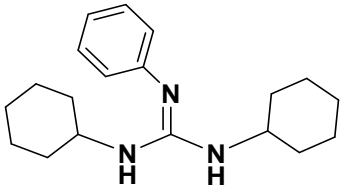
Yield: 86%. ^{1}H-NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.18 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 3.38 (br, 2H), 1.98 (d, J = 9.0 Hz, 4H), 1.70 - 1.57 (m, 6H), 1.40 - 1.28 (m, 4H), 1.20 - 1.02 (m, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.20, 149.28, 129.31, 126.31, 125.02, 50.21, 33.88, 25.76, 25.00 ppm. The NMR data are in accordance with the literature.[2]

***N*-(4-nitrophenyl)-*N'*, *N"*-dicyclohexylguanidine (3p)**



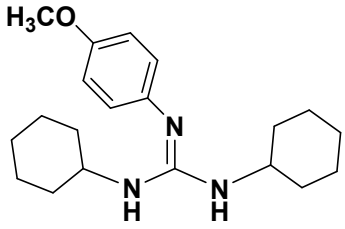
Yield: 77%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 8.08 (d, J = 6.0 Hz, 2H), 6.87 (d, J = 6.0 Hz, 2H), 3.41 (bs, 2H), 1.96 (bs, 4H), 1.83-1.58 (m, 6H), 1.34 - 1.31 (m, 4H), 1.15 (bs, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 158.53, 150.46, 140.74, 125.60, 122.76, 50.27, 33.60, 25.53, 24.82 ppm. The NMR data are in accordance with the literature.[2]

***N*-phenyl-*N'*, *N"*-dicyclohexylguanidine (3q)**



Yield: 83%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 7.23 - 7.21 (m, 2H), 6.93 - 6.88 (m, 1H), 6.86 - 6.84 (m, 2H), 3.62 (br, 2H), 3.41 (br, 2H), 2.00 (d, J = 12.0 Hz, 4H), 1.70 - 1.57 (m, 6H), 1.40 - 1.28 (m, 4H), 1.20 - 1.03 (m, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 150.55, 150.10, 129.32, 123.73, 121.39, 50.24, 33.91, 25.80, 25.03 ppm. The NMR data are in accordance with the literature.[5]

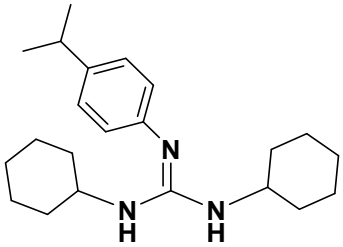
***N*-(4-methoxyphenyl)-*N'*, *N"*-dicyclohexylguanidine (3r)**



Yield: 87%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 6.81 - 6.74 (m, 4H), 3.75 (s, 3H), 3.38 (bs, 2H), 1.98 (d, J = 12.0 Hz, 4H), 1.68 - 1.56 (m, 6H), 1.39 - 1.27 (m, 4H), 1.19 - 1.00 (m, 6H) ppm.

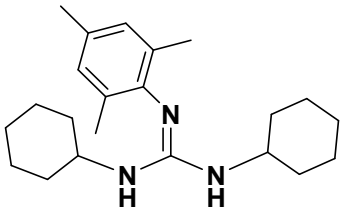
$^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 154.59, 150.60, 143.54, 124.39, 114.67, 55.52, 50.19, 33.92, 25.79, 25.01 ppm. The NMR data are in accordance with the literature.[5]

_N_-(4-isopropylphenyl)-_N'_, _N"_-dicyclohexylguanidine (3s)



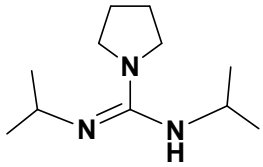
Yield: 84%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 6.96 (d, J = 6.0 Hz, 2H), 6.57 (d, J = 9.0 Hz, 2H), 3.17 (bs, 2H), 2.81 - 2.69 (m, 1H), 1.89 (d, J = 9.0 Hz, 4H), 1.71 (d, J = 3.0 Hz, 4H), 1.54 (d, J = 9.0 Hz, 2H), 1.36 - 1.27 (m, 10H), 1.17 (d, J = 6.0 Hz, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 144.10, 139.44, 138.46, 126.76, 114.86, 55.43, 34.71, 33.01, 25.25, 24.44, 24.01 ppm. The NMR data are in accordance with the literature.[2]

_N_-(2,4,6-trimethylphenyl)-_N'_, _N"_-dicyclohexylguanidine (3t)



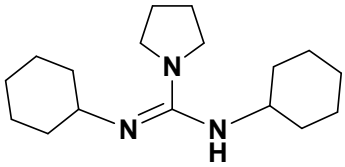
Yield: 76%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 6.77 (s, 2H), 3.20 (br, 2H), 2.21 (s, 3H), 2.16 (s, 6H), 1.94 - 1.91 (m, 4H), 1.76 (br, 4H), 1.59 - 1.56 (m, 2H), 1.39 - 1.24 (m, 10H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 140.10, 139.91, 128.88, 127.20, 121.89, 55.82, 35.00, 25.53, 24.77, 20.42, 17.61 ppm. The NMR data are in accordance with the literature.[3]

***N,N′*-diisopropylpyrrolidine-1-carboximidamide (3u)**



Yield: 84%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 3.34 - 3.30 (m, 2H), 3.19 (br, 4H), 1.72 (br, 4H), 1.04 (d, J = 6.0 Hz, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 153.26, 47.62, 46.35, 24.93, 24.48 ppm. The NMR data are in accordance with the literature.[2]

***N,N′*-dicyclohexylpyrrolidine-1-carboximidamide (3v)**



Yield: 81%. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ_H 3.22 (br, 4H), 2.93 (br, 2H), 1.76 - 1.70 (m, 12H), 1.59 - 1.55 (m, 2H), 1.31-1.02 (m, 10H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$): δ_c 153.55, 55.21, 47.99, 35.29, 25.83, 25.62, 25.25 ppm. The NMR data are in accordance with the literature.[2]

^{1}H NMR and ^{13}C{^{1}H} NMR spectra of guanidine product:

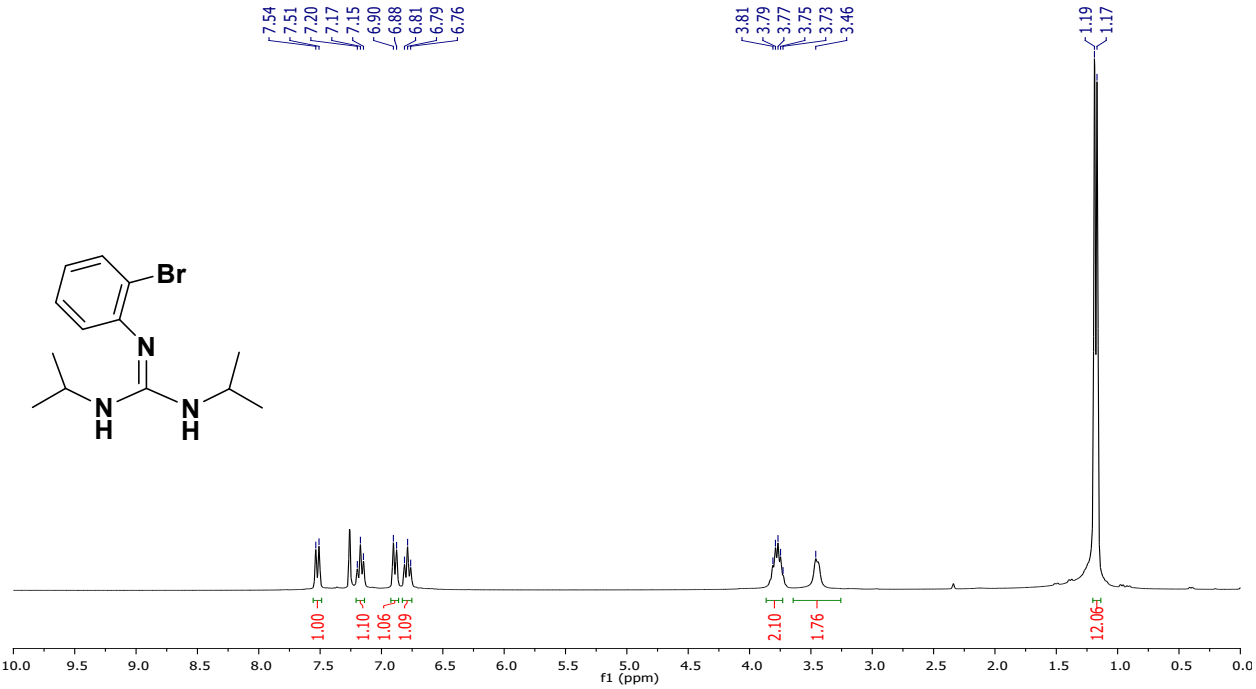


Figure FS16. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3a**.

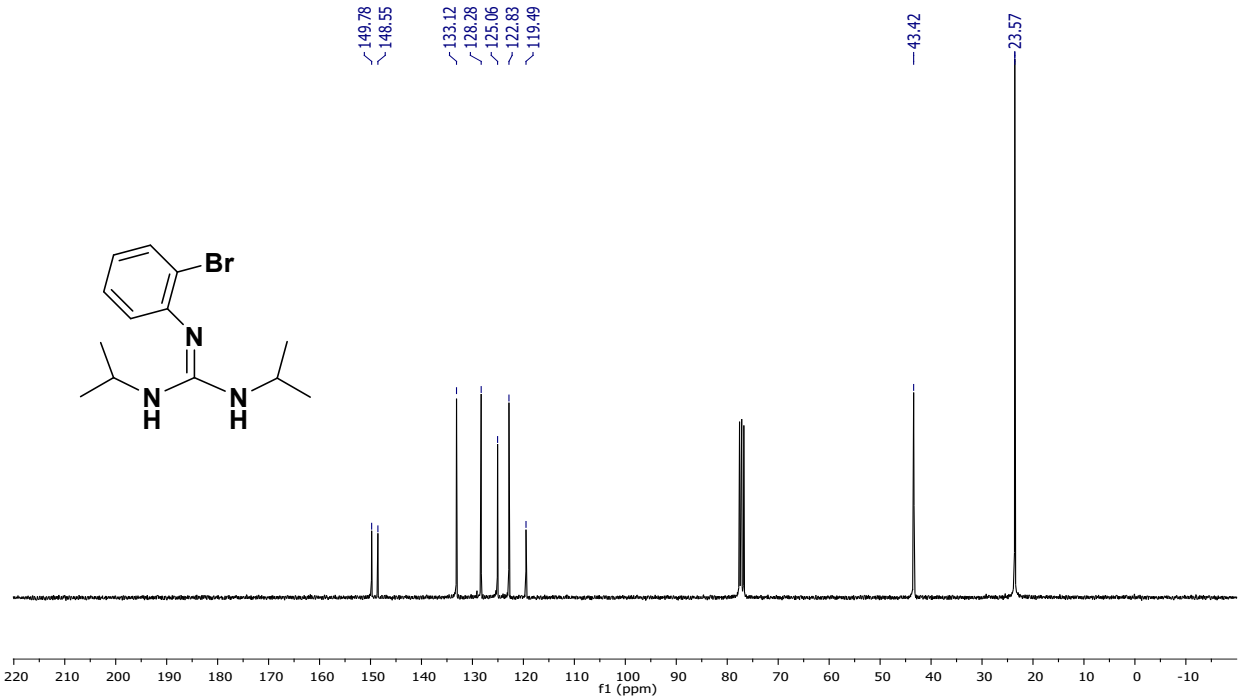


Figure FS17. ^{13}C{^{1}H} NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3a**.

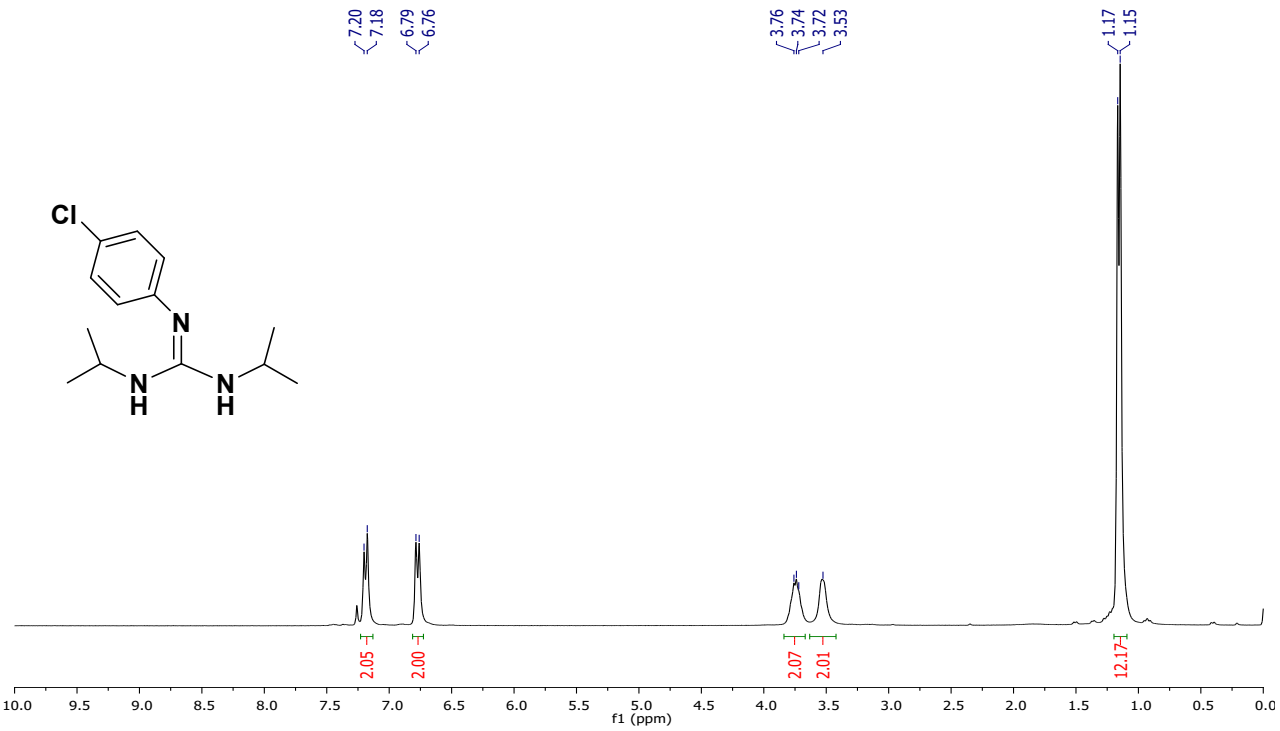


Figure FS18. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3b**.

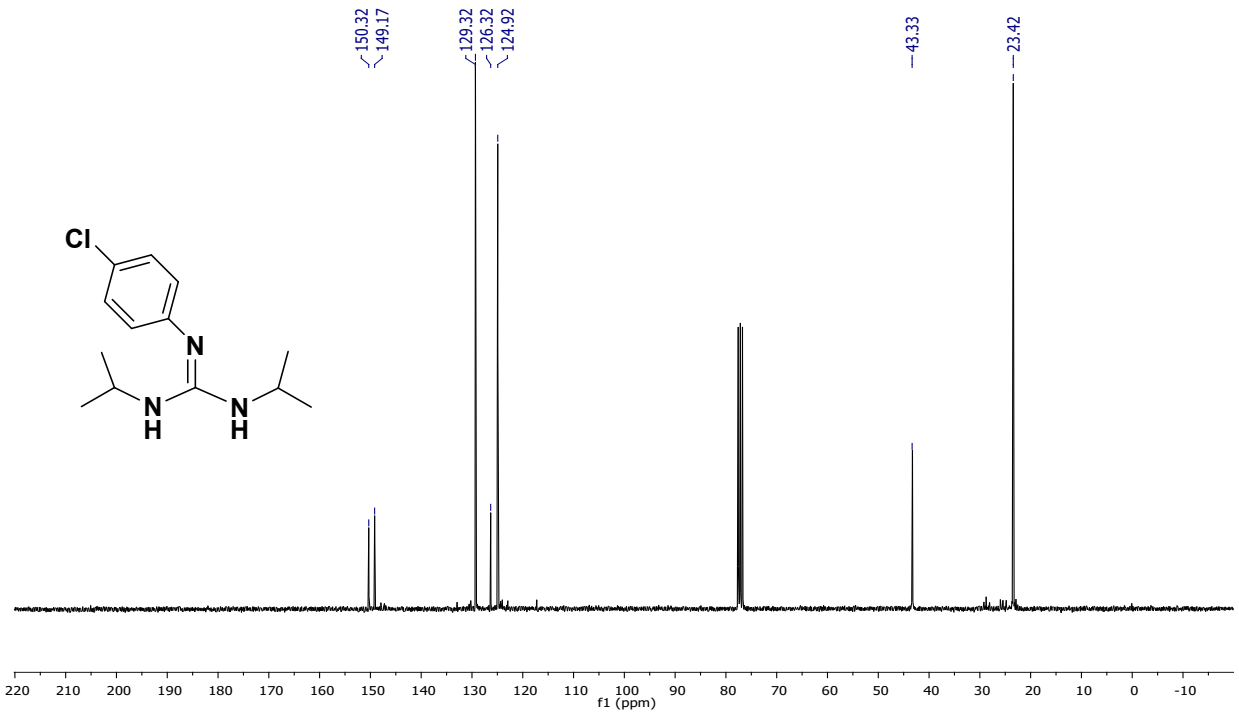


Figure FS19. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3b**.

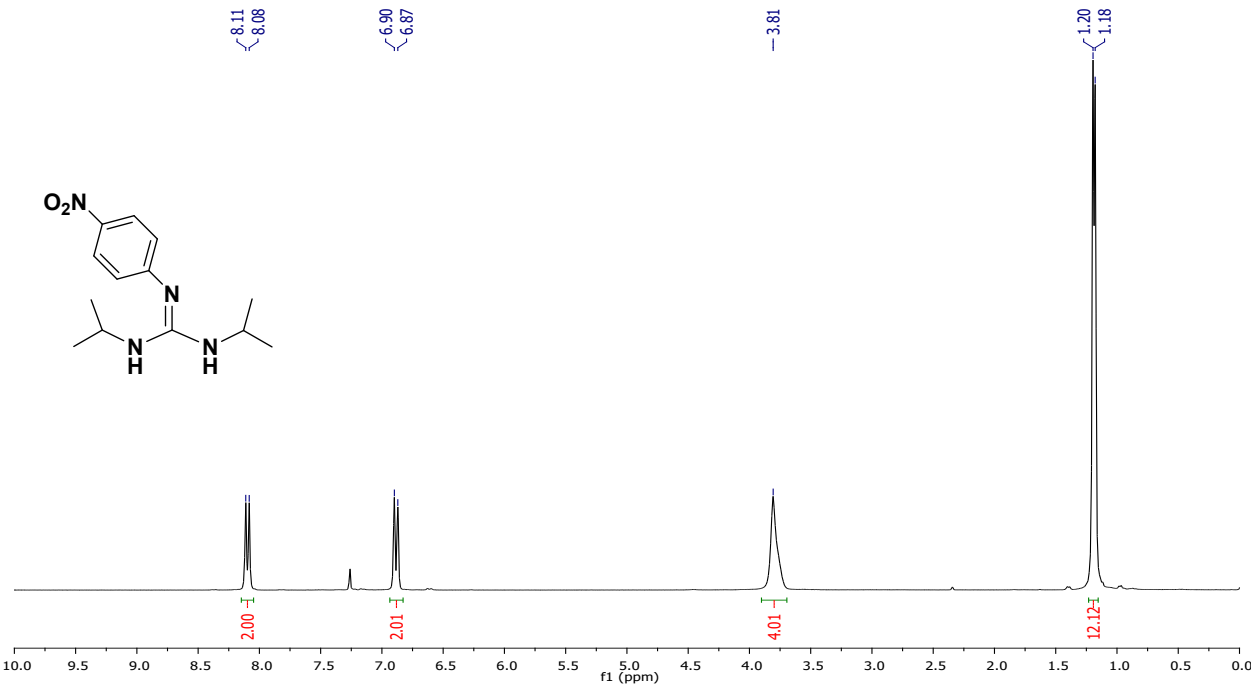


Figure FS20. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3c**.

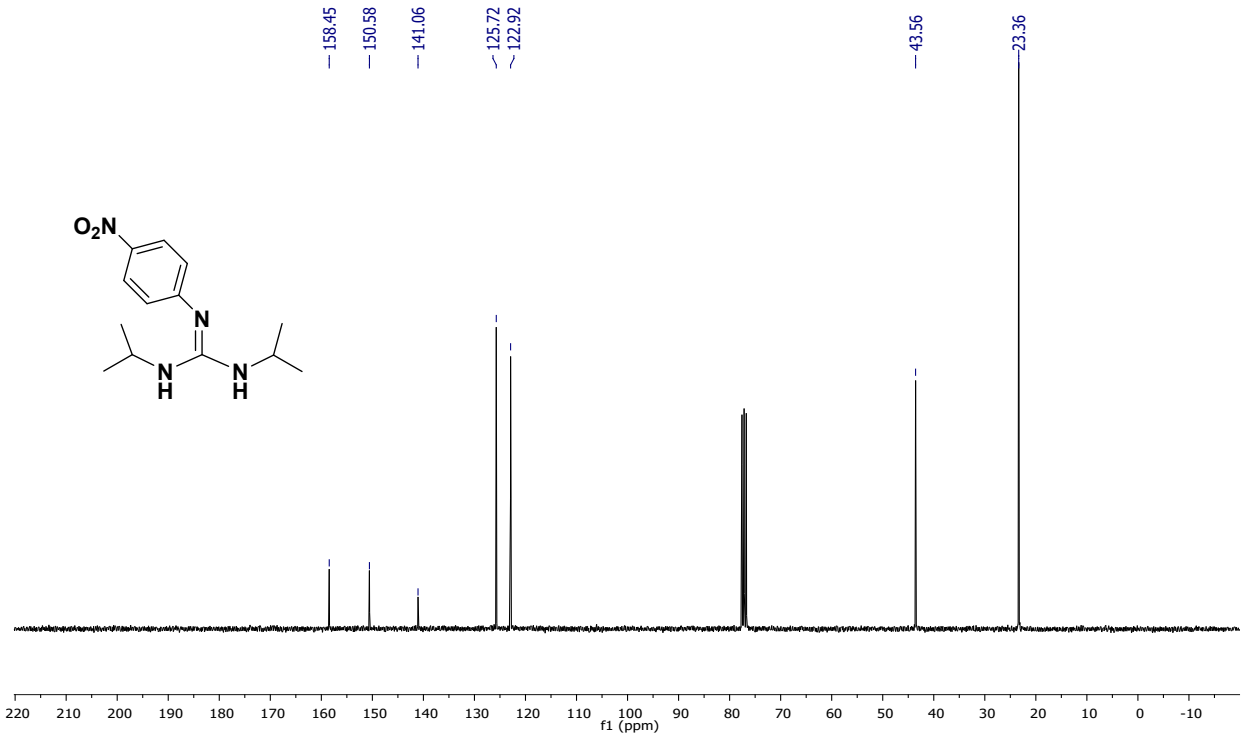


Figure FS15. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3c**.

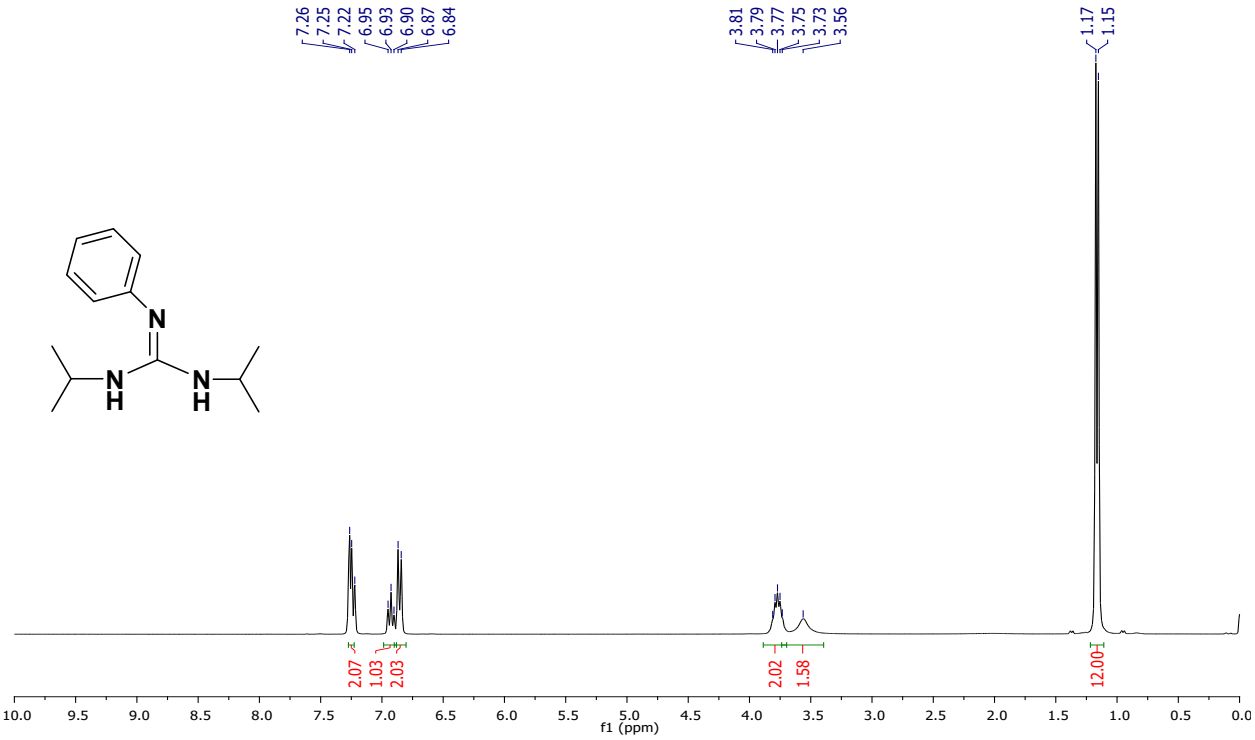


Figure FS16. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3d**.

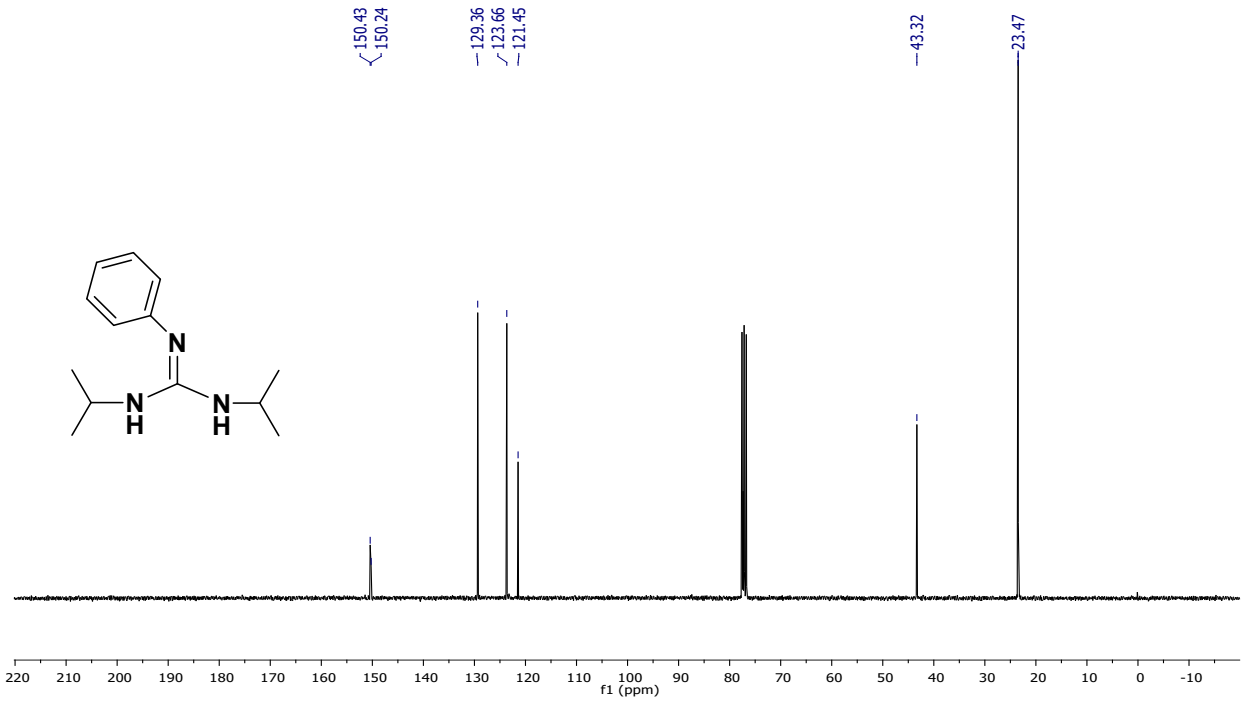


Figure FS17. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3d**.

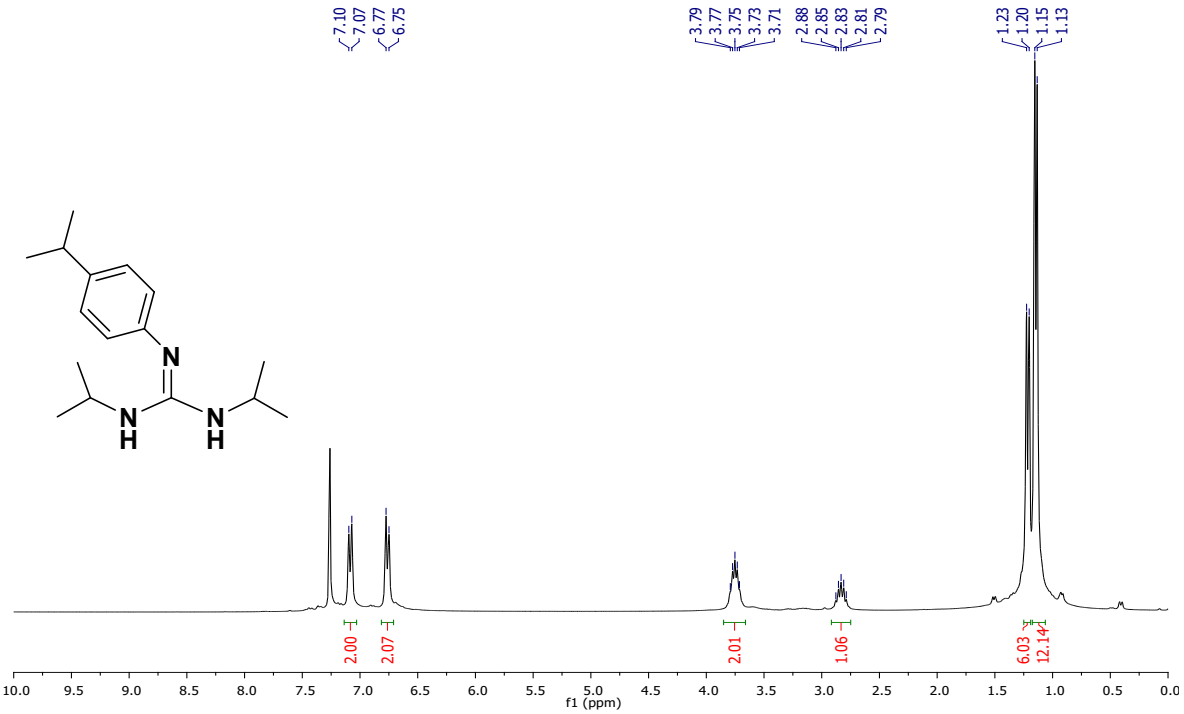


Figure FS18. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3e**.

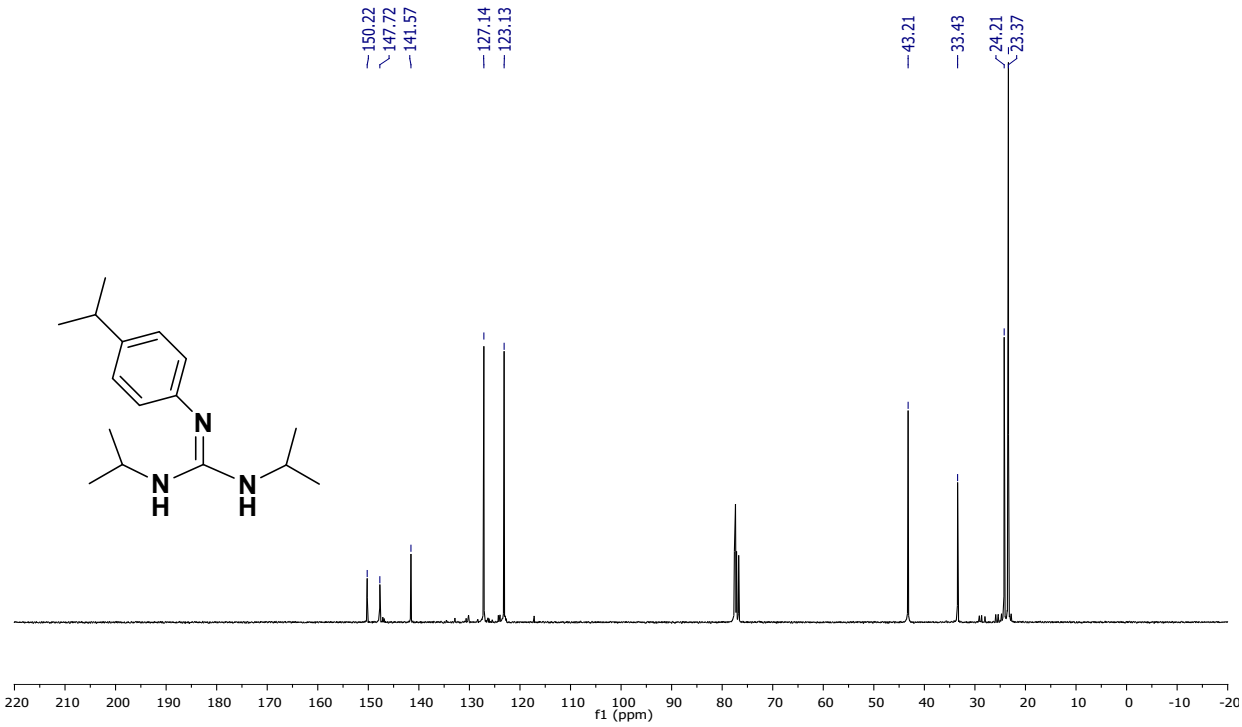


Figure FS19. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3e**.

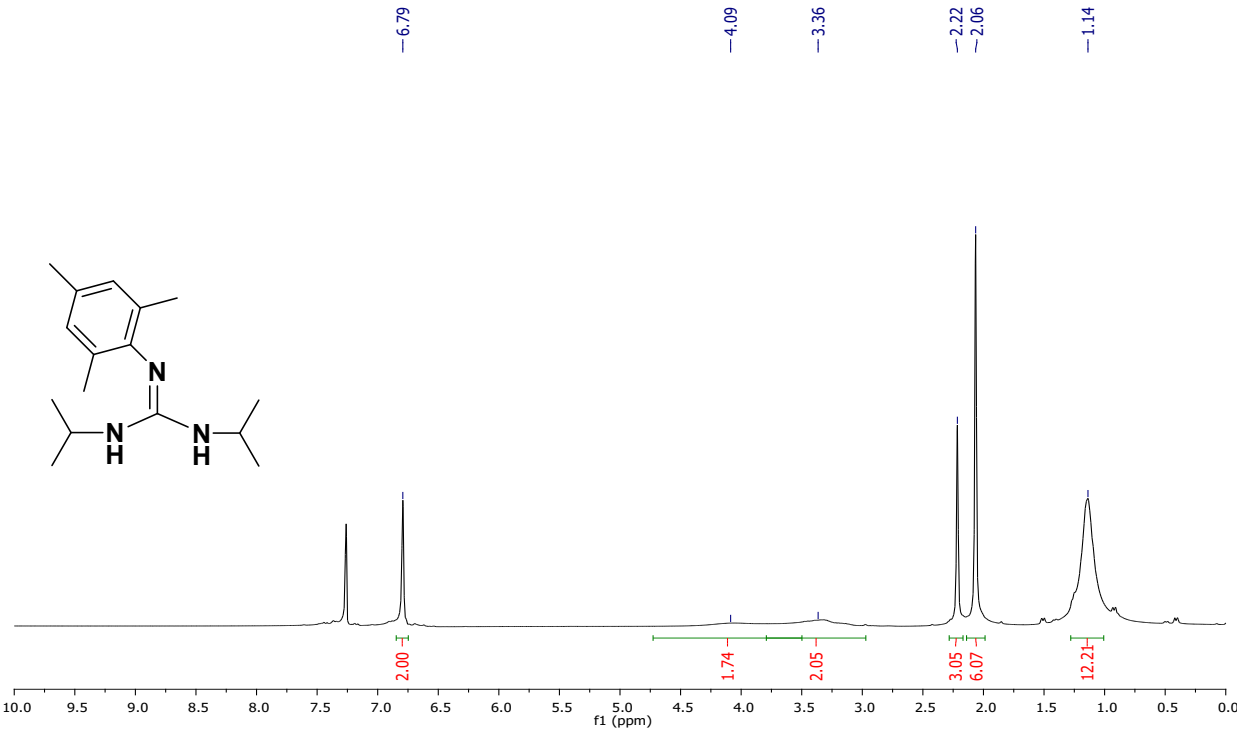


Figure FS20. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3f**.

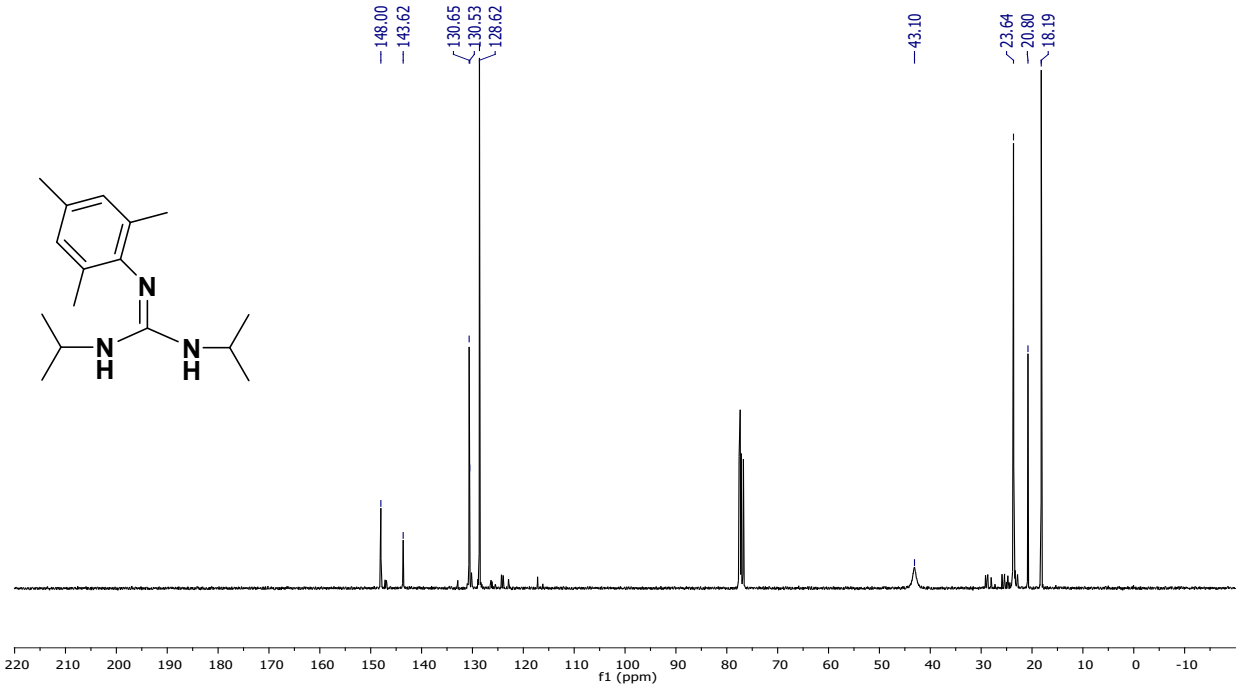


Figure FS21. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3f**.

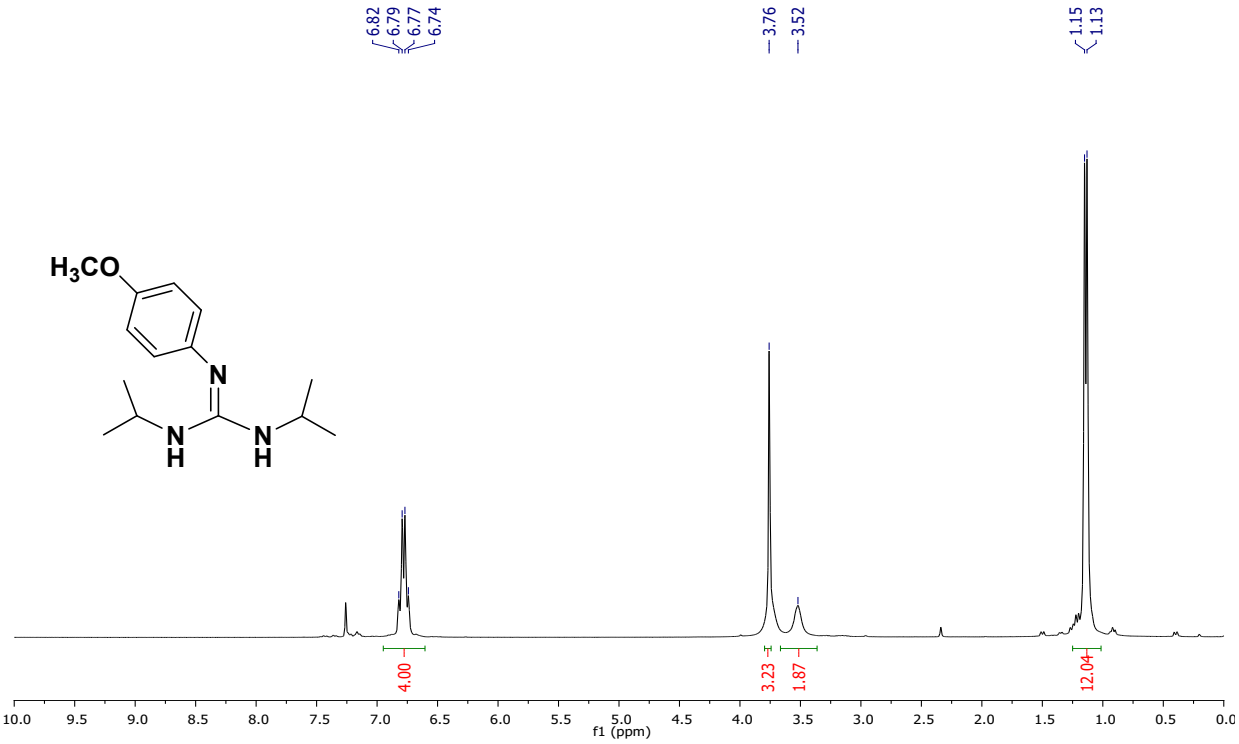


Figure FS22. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3g**.

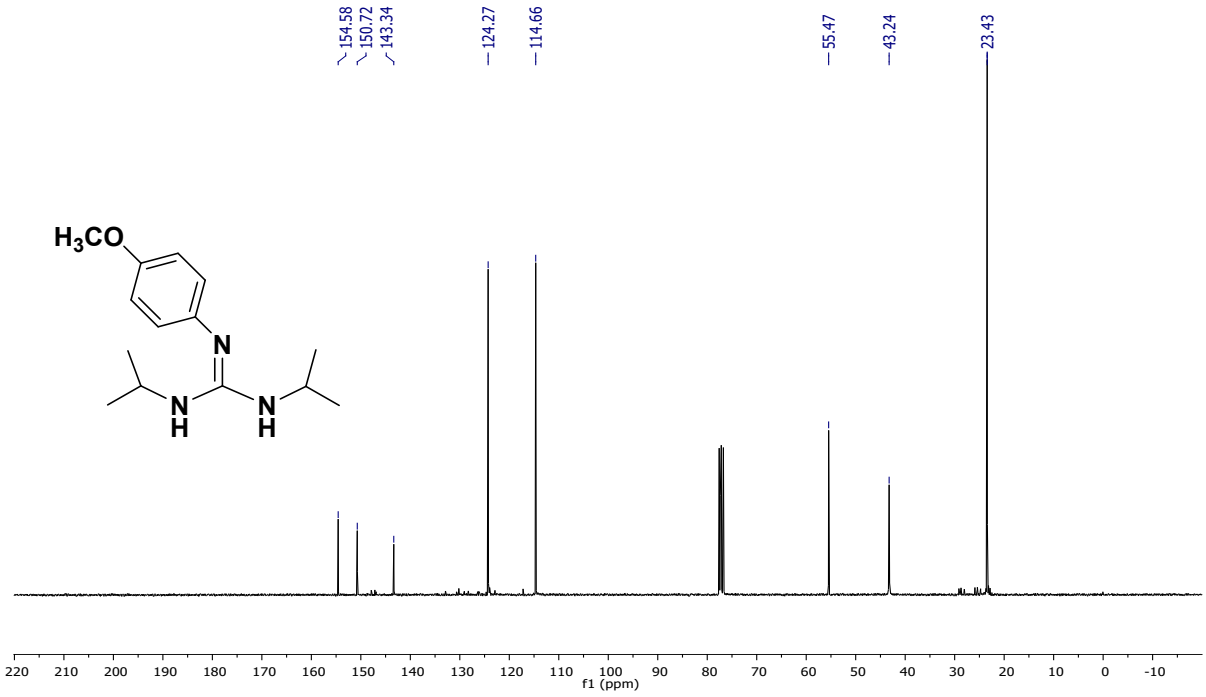


Figure FS23. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3g**

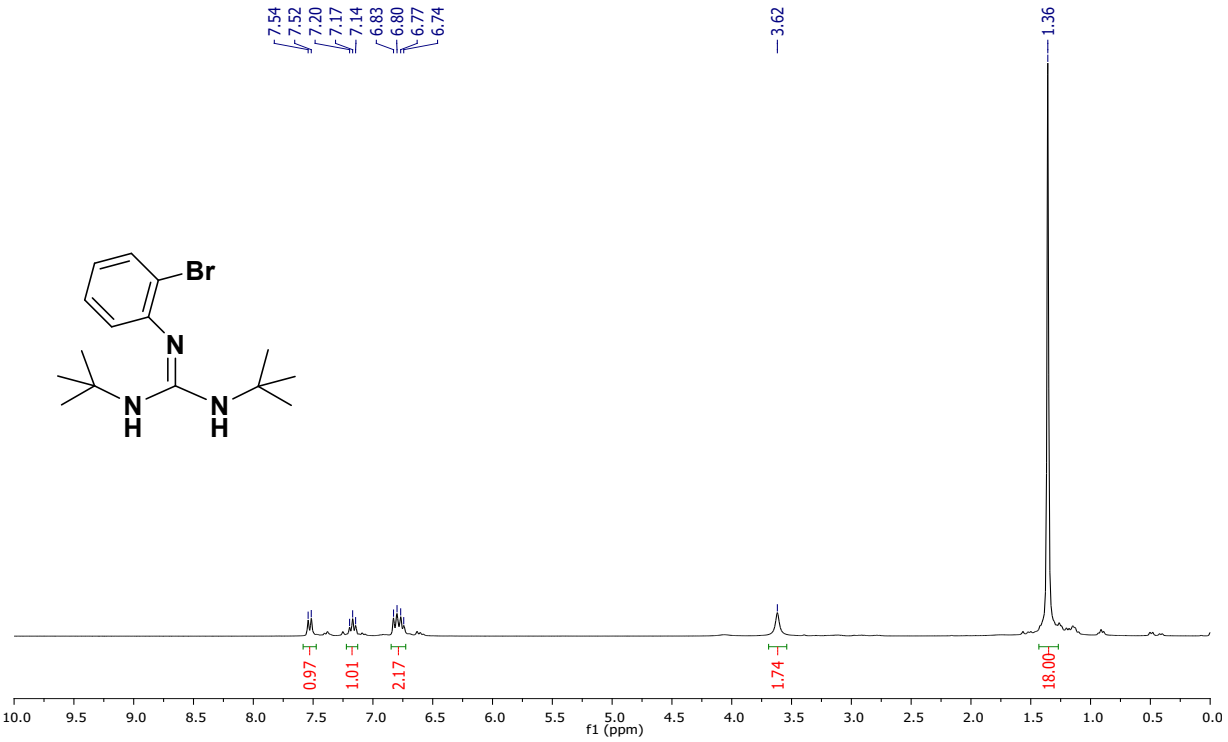


Figure FS24. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3h**.

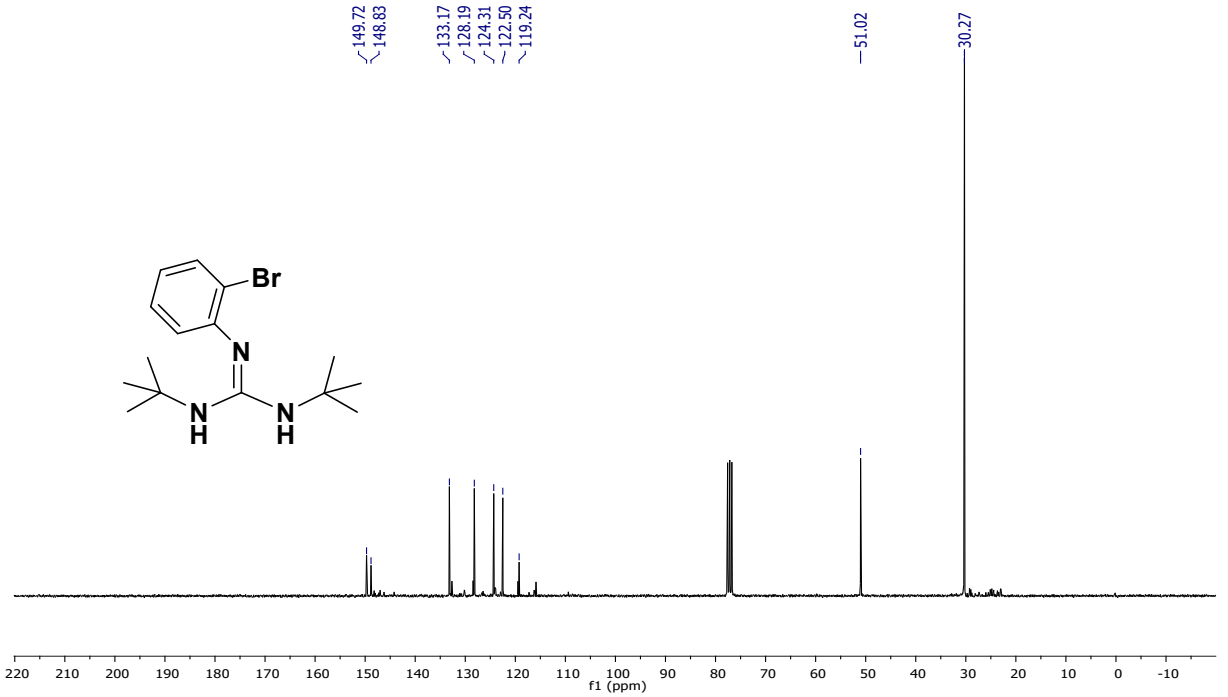


Figure FS25. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3h.**

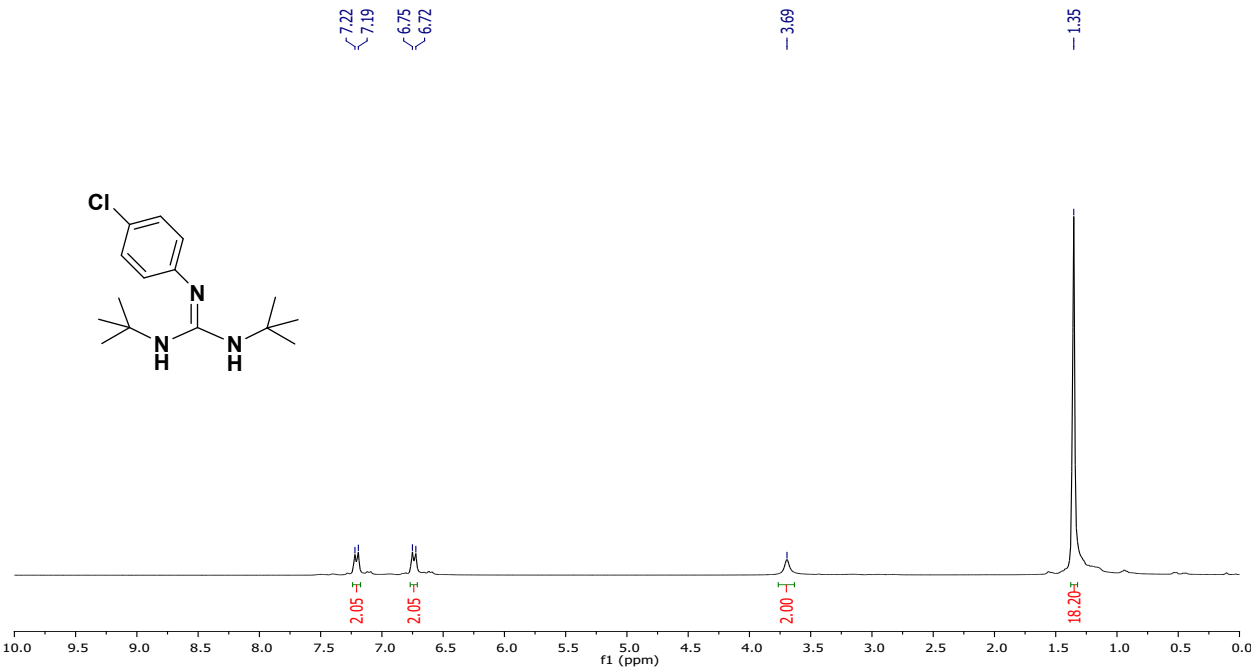


Figure FS26. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3i**.

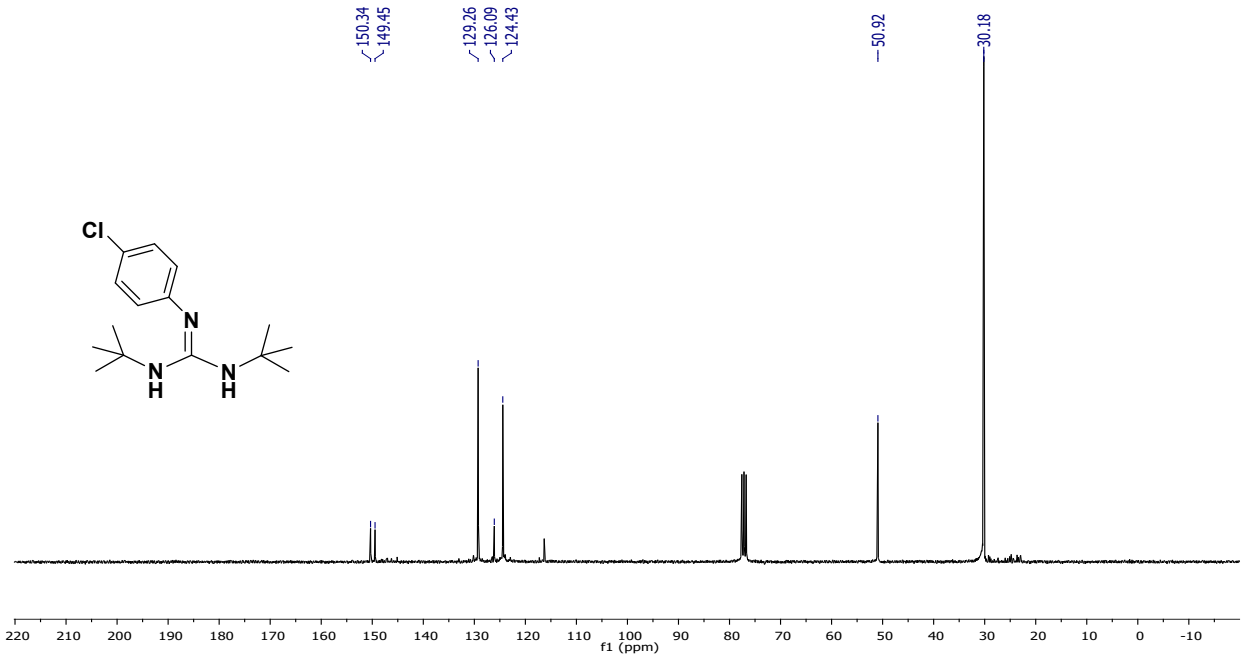


Figure FS27. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3i.**

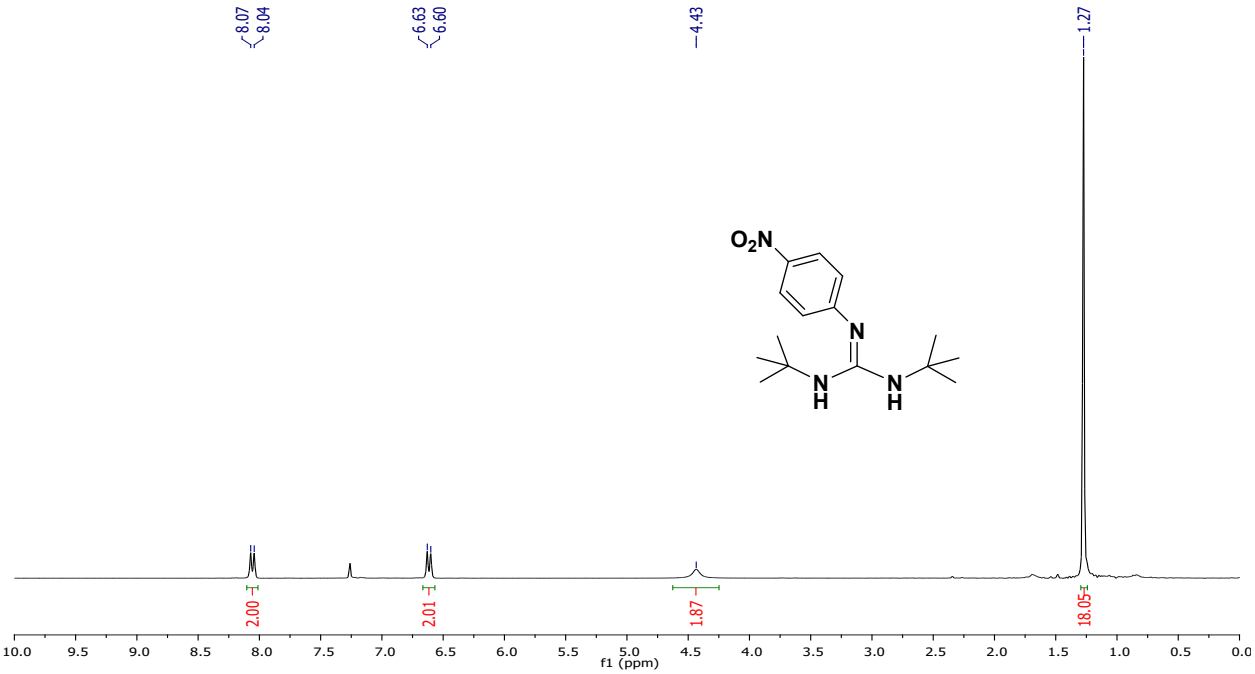


Figure FS28. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3j**.

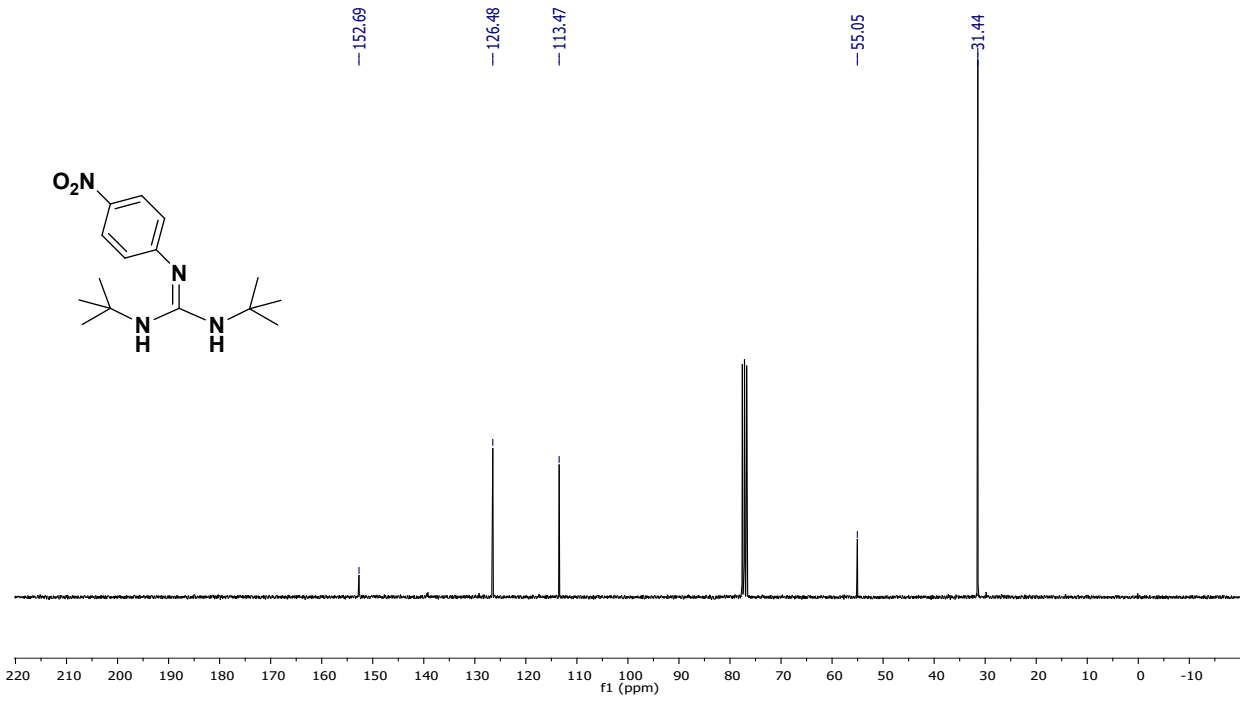


Figure FS29. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3j.**

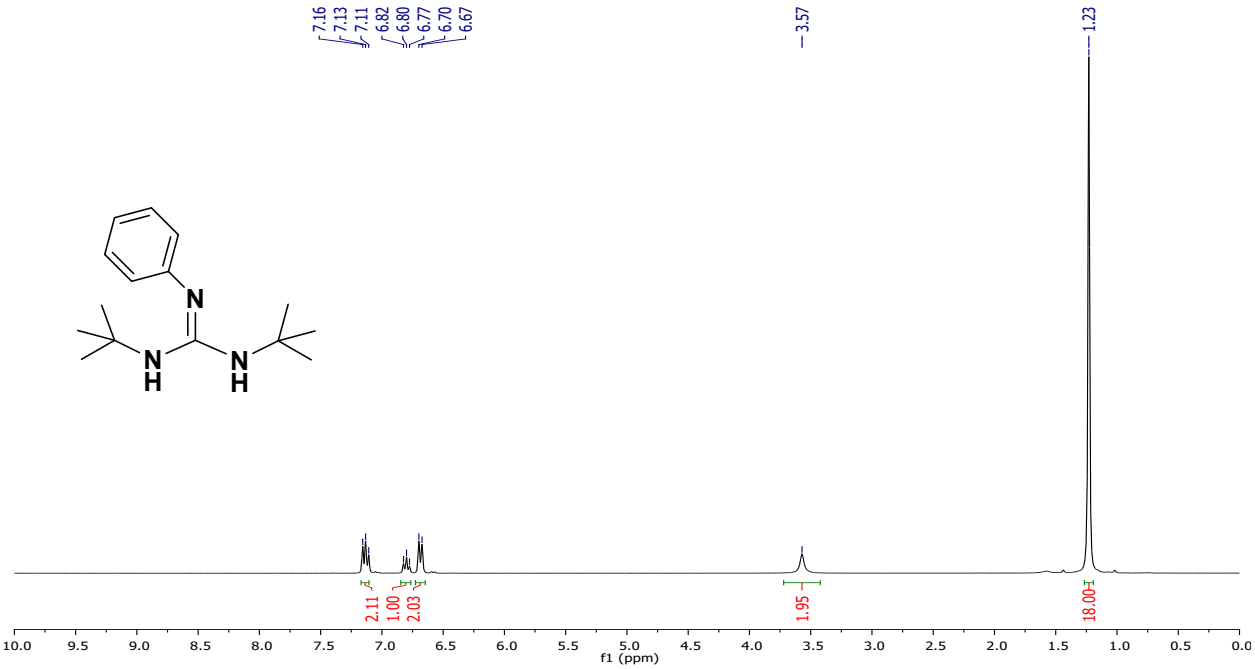


Figure FS30. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3k**.

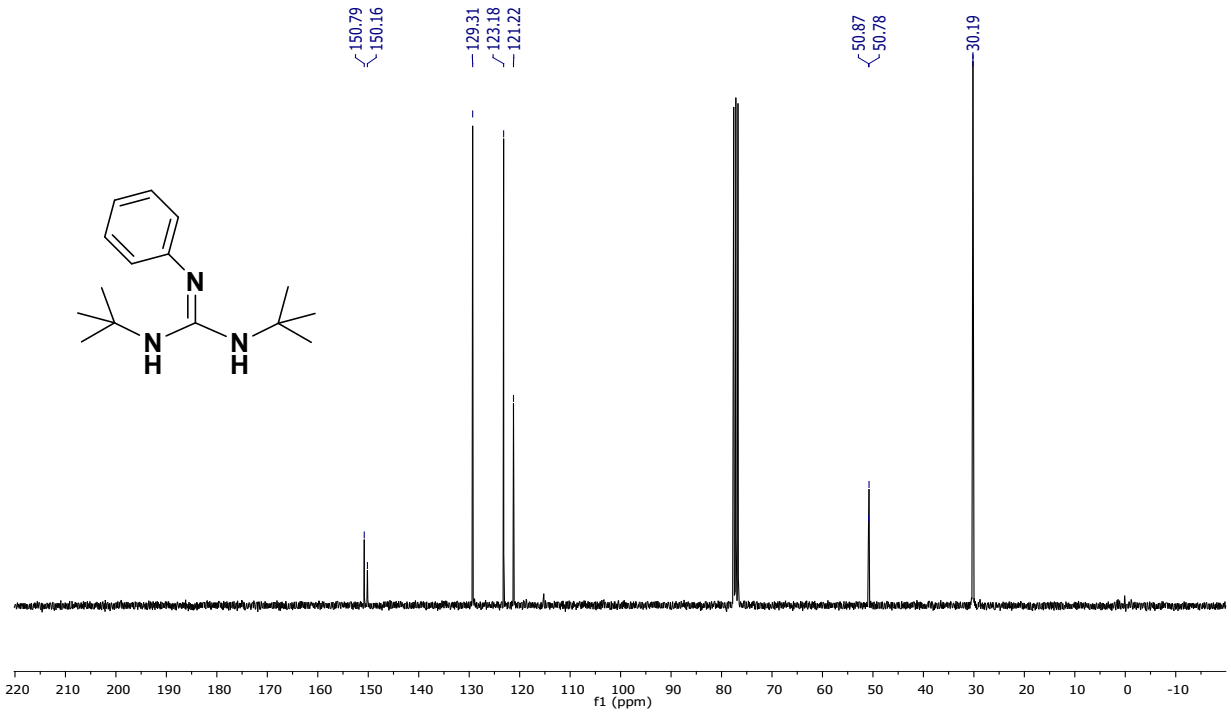


Figure FS31. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3k.**

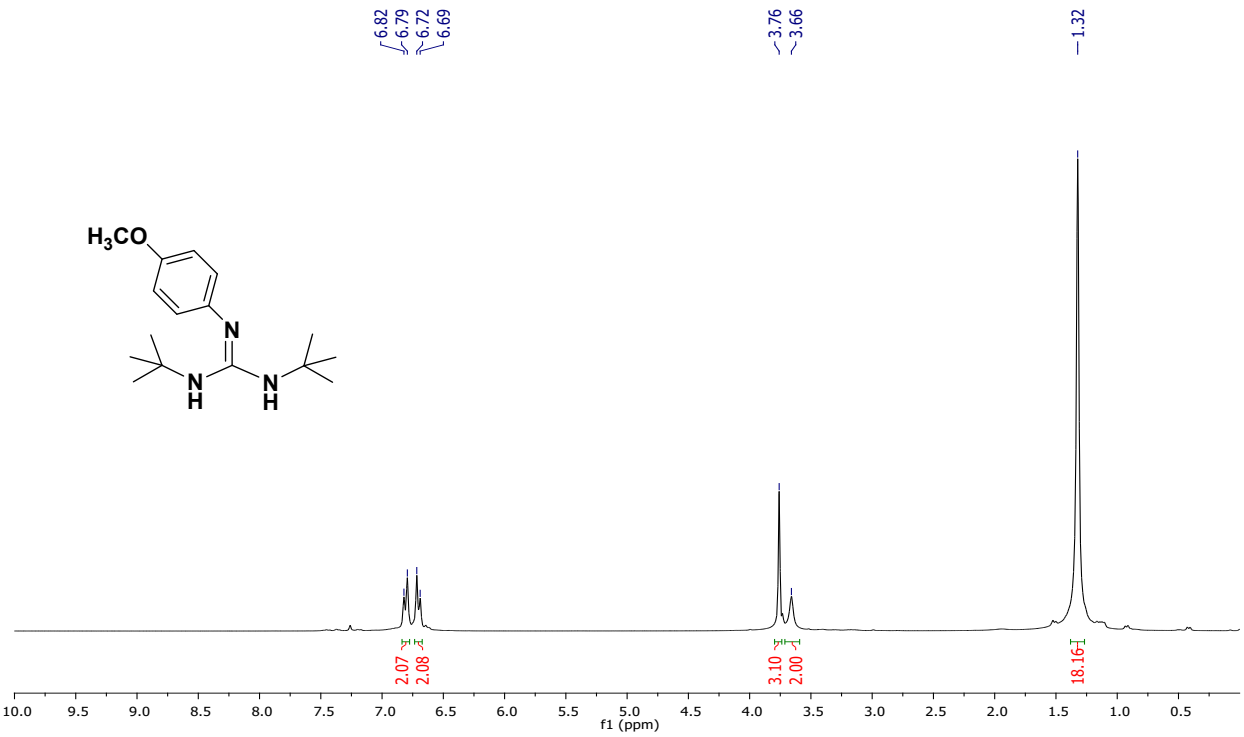


Figure FS32. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3l**.

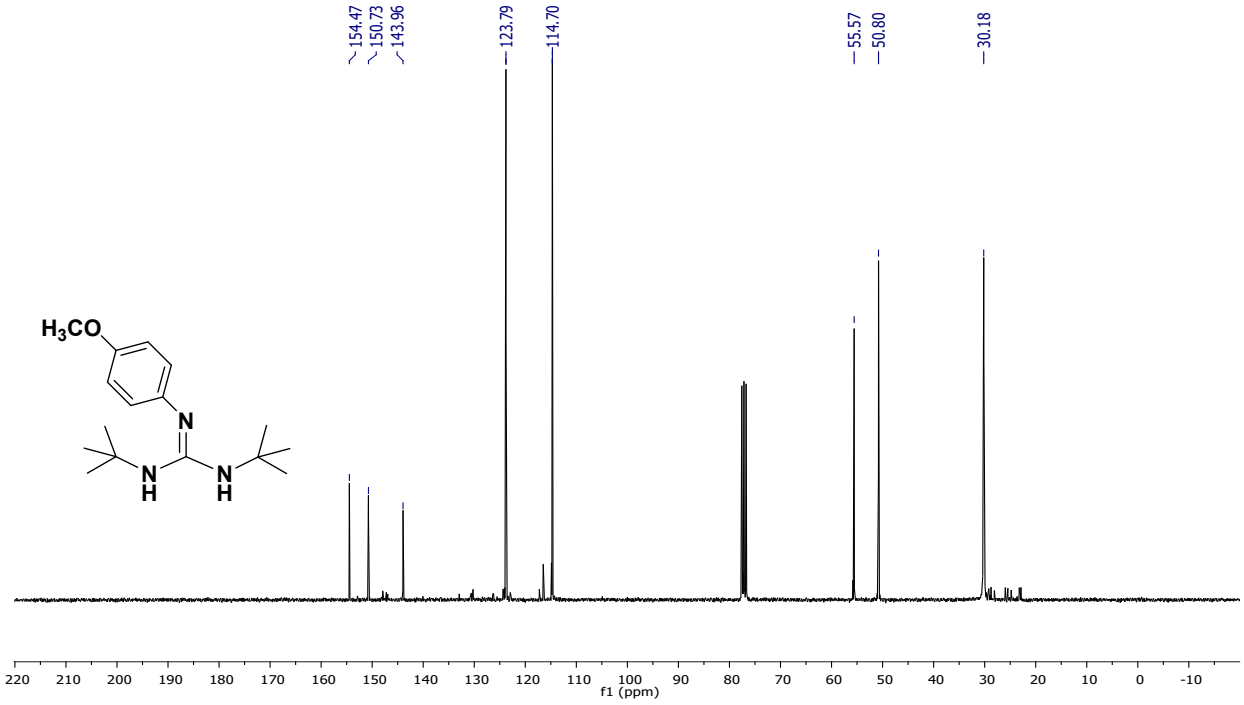


Figure FS33. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3l.**

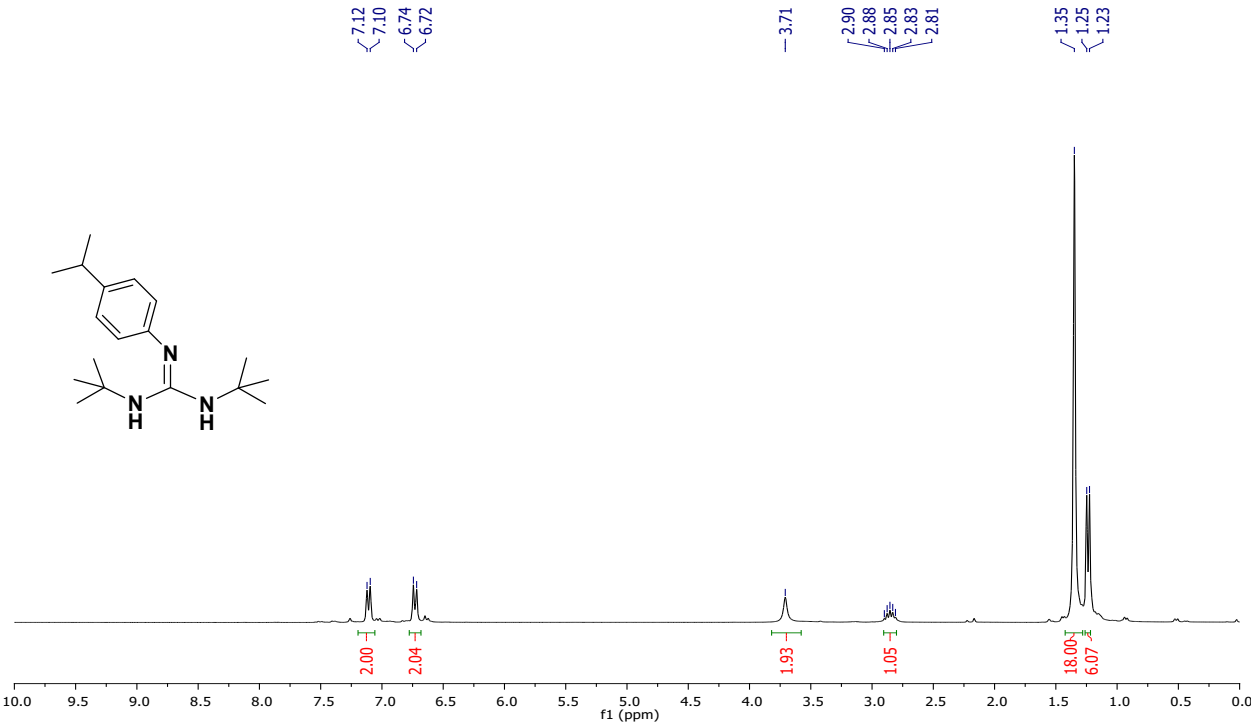


Figure FS34. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3m**.

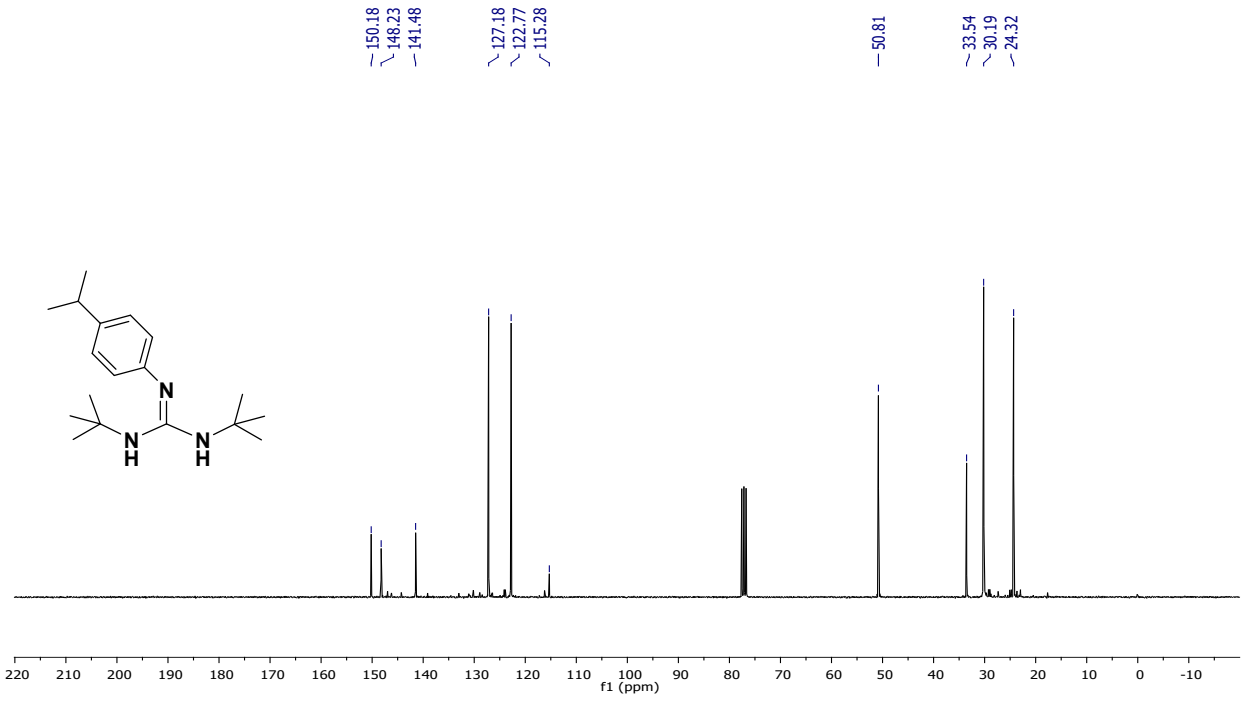


Figure FS35. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3m.**

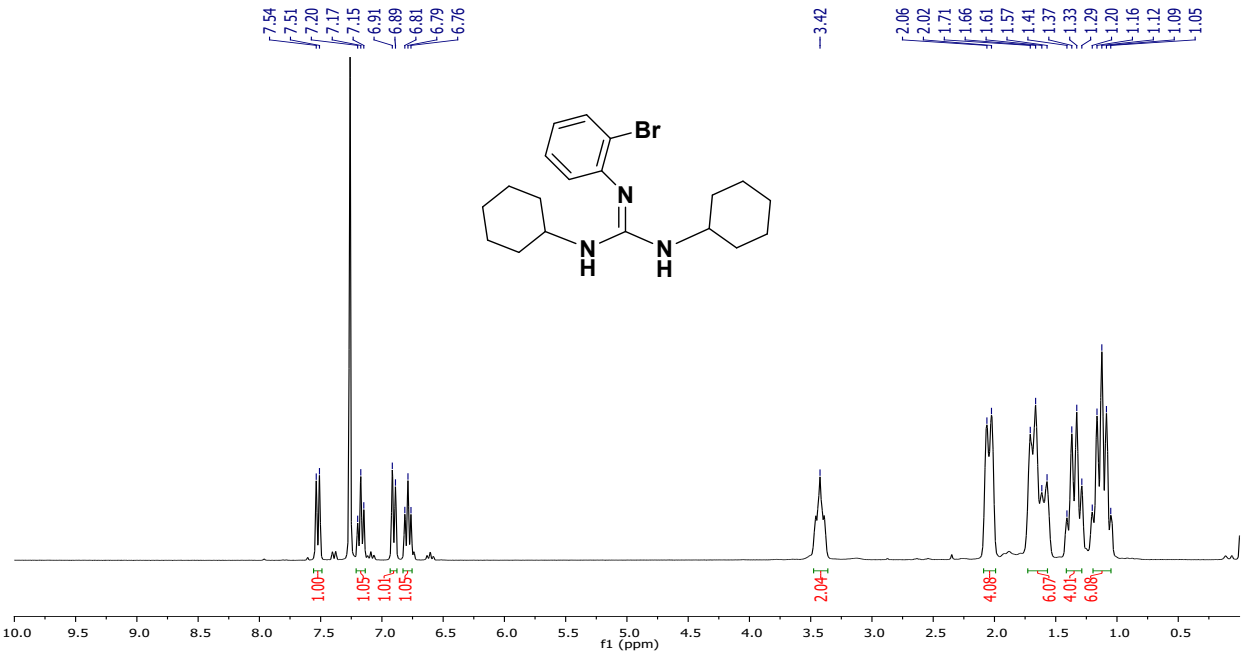


Figure FS36. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3n**.

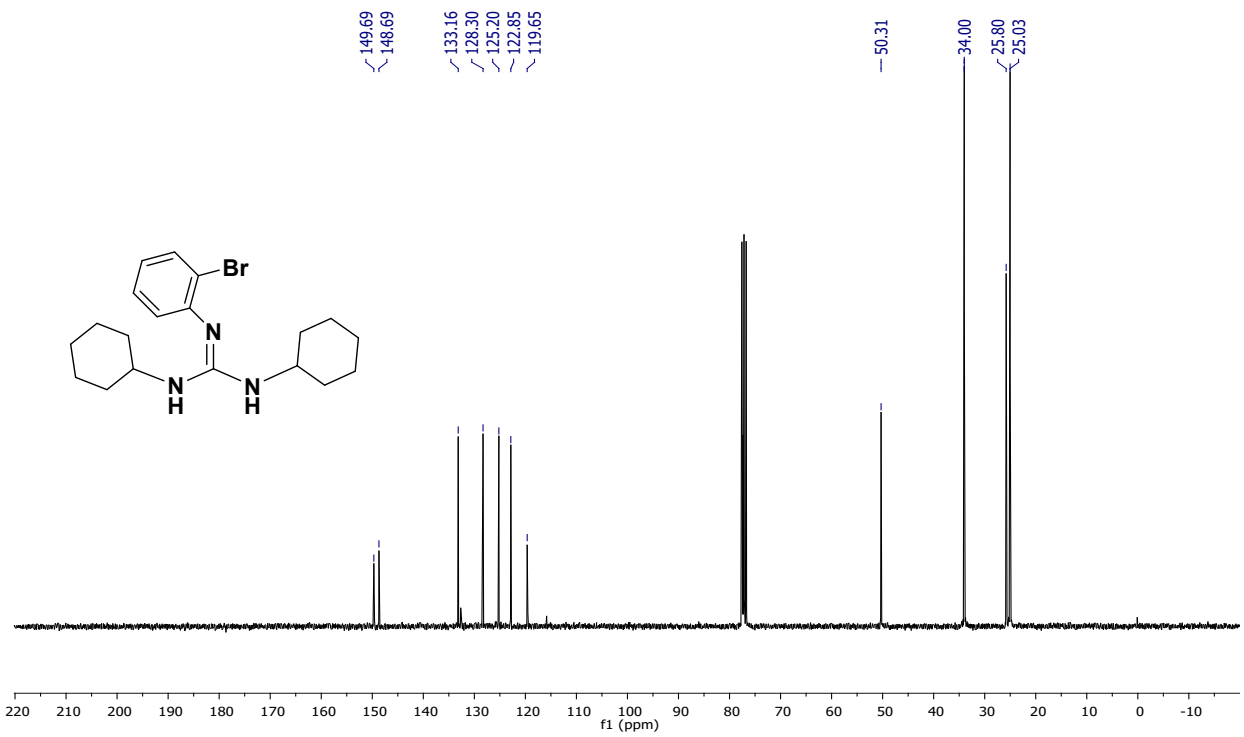


Figure FS37. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3n.**

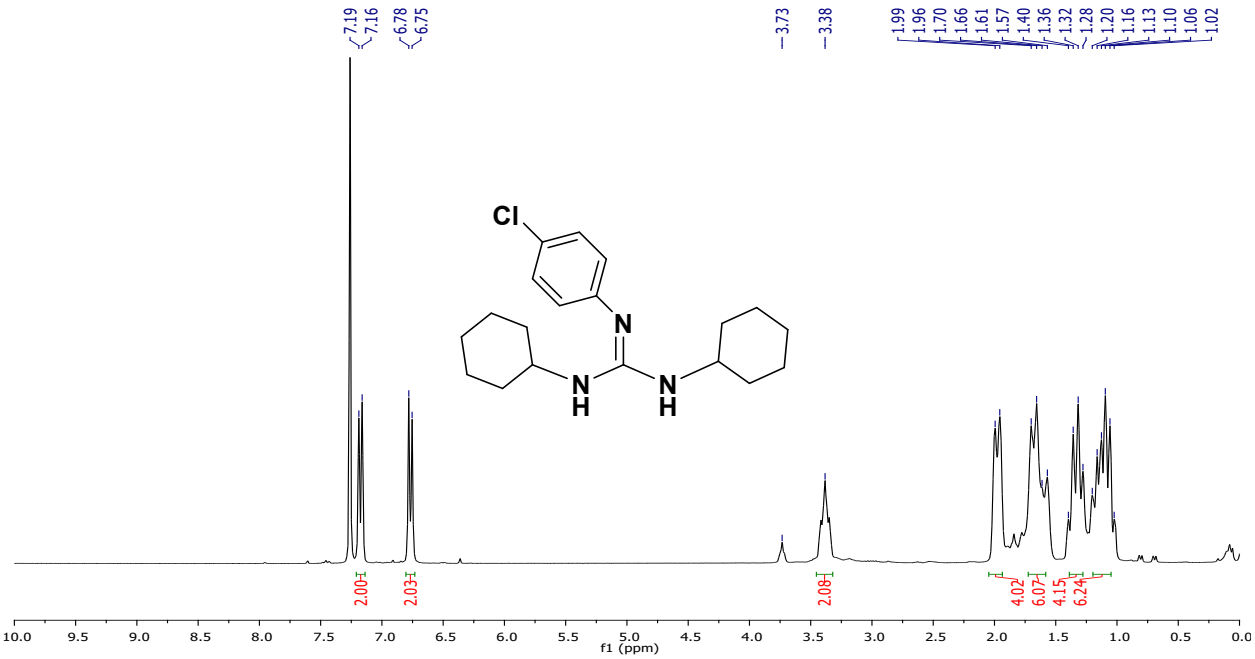


Figure FS38. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3o**.

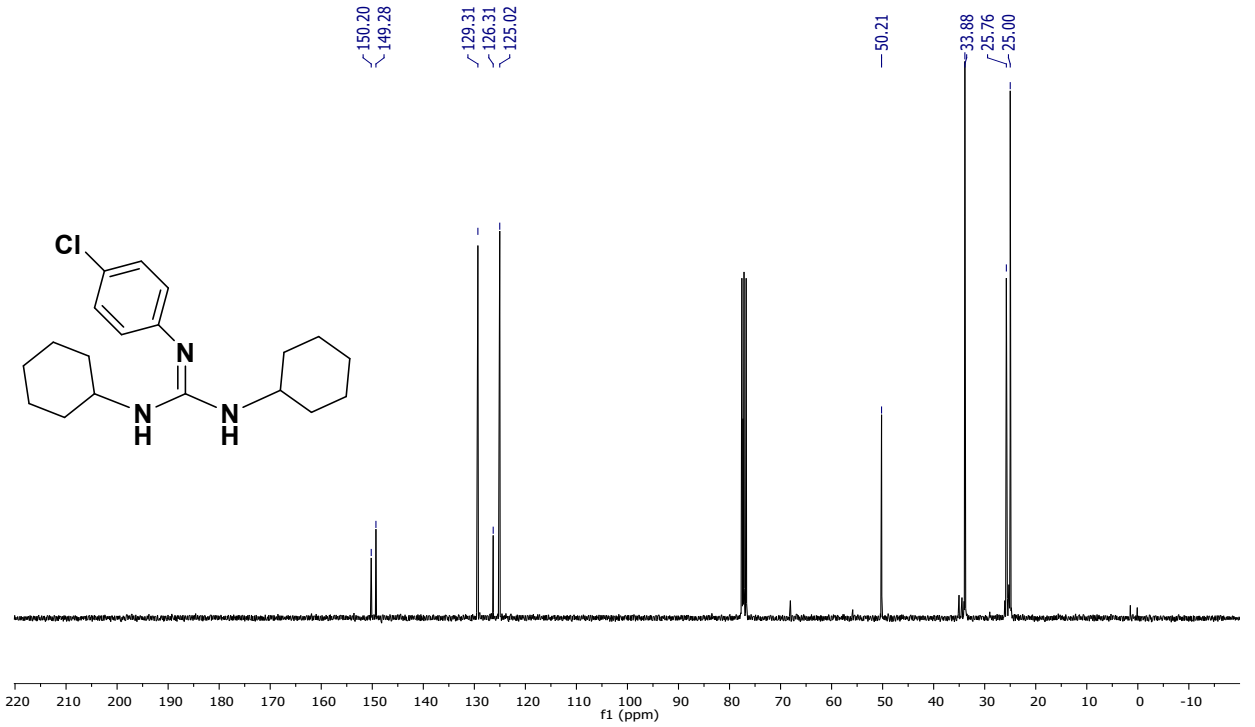


Figure FS39. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3o.**

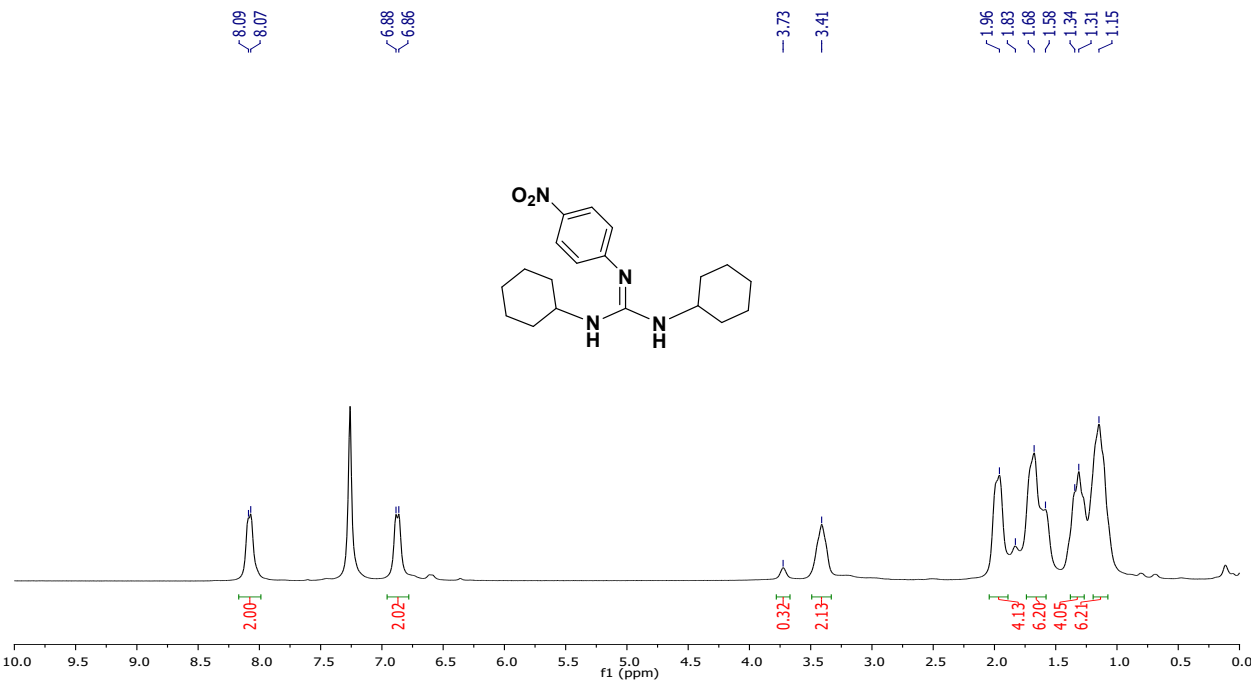


Figure FS40. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3p**.

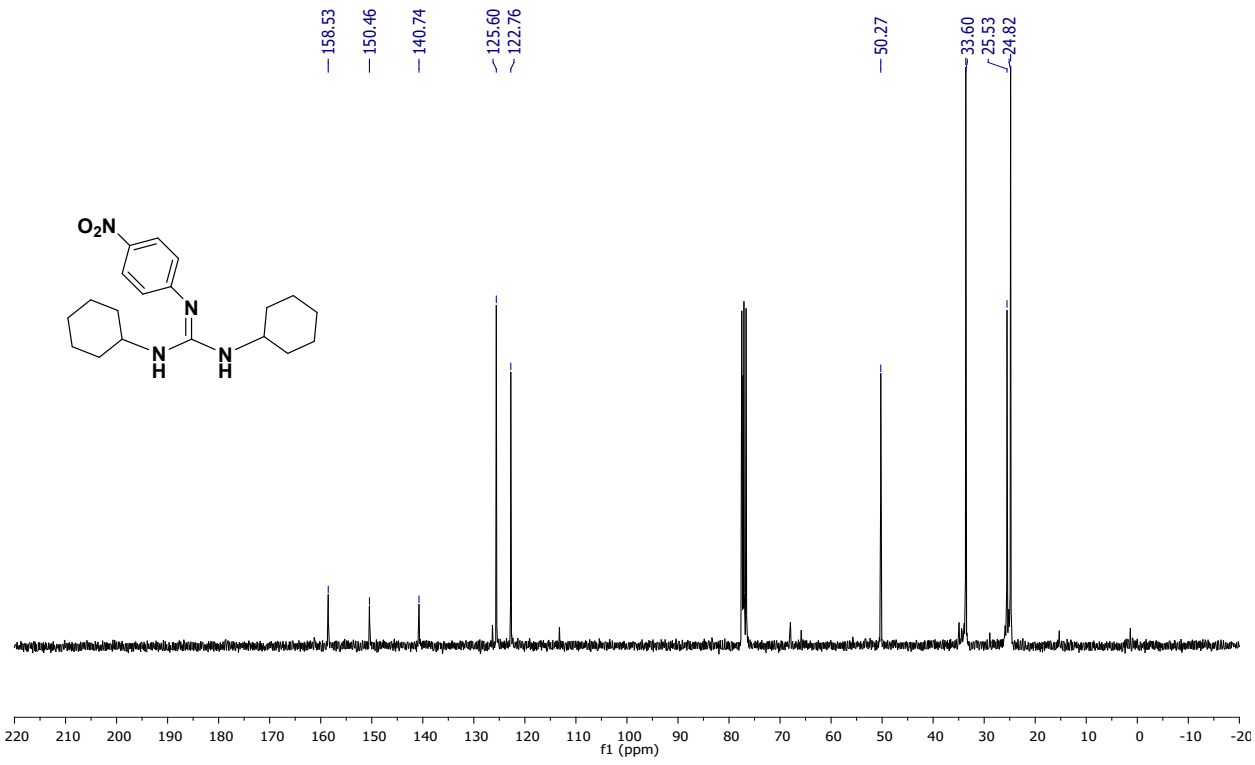


Figure FS41. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3p.**

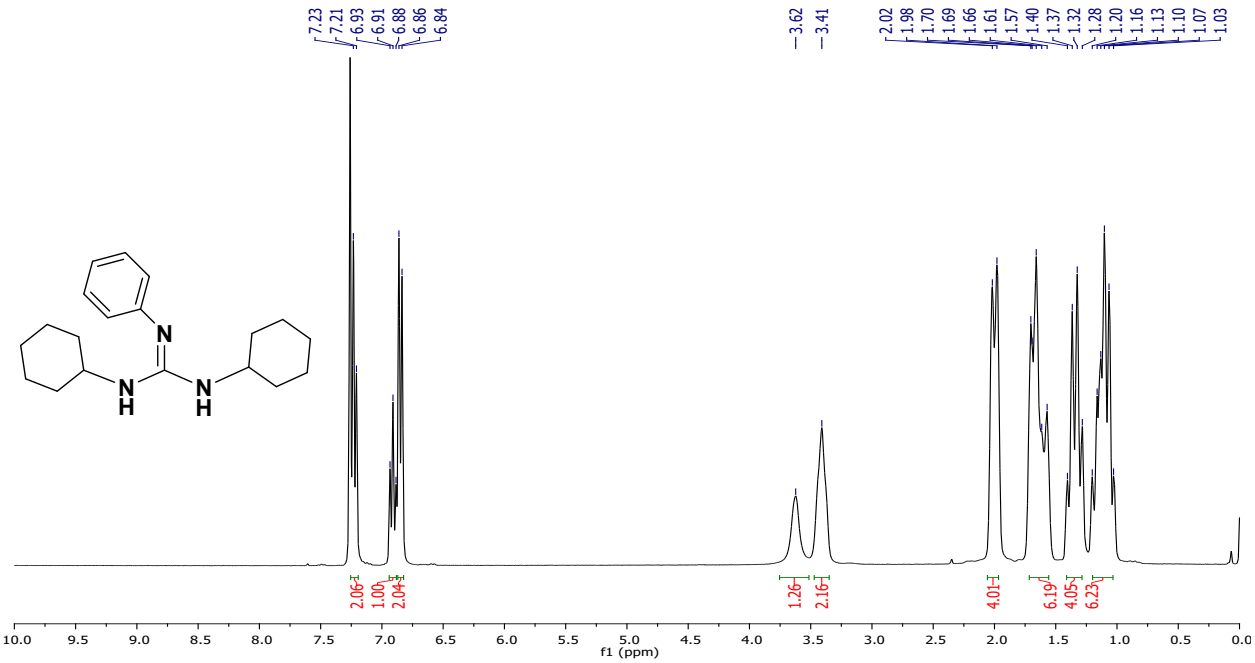


Figure FS42. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3q**.

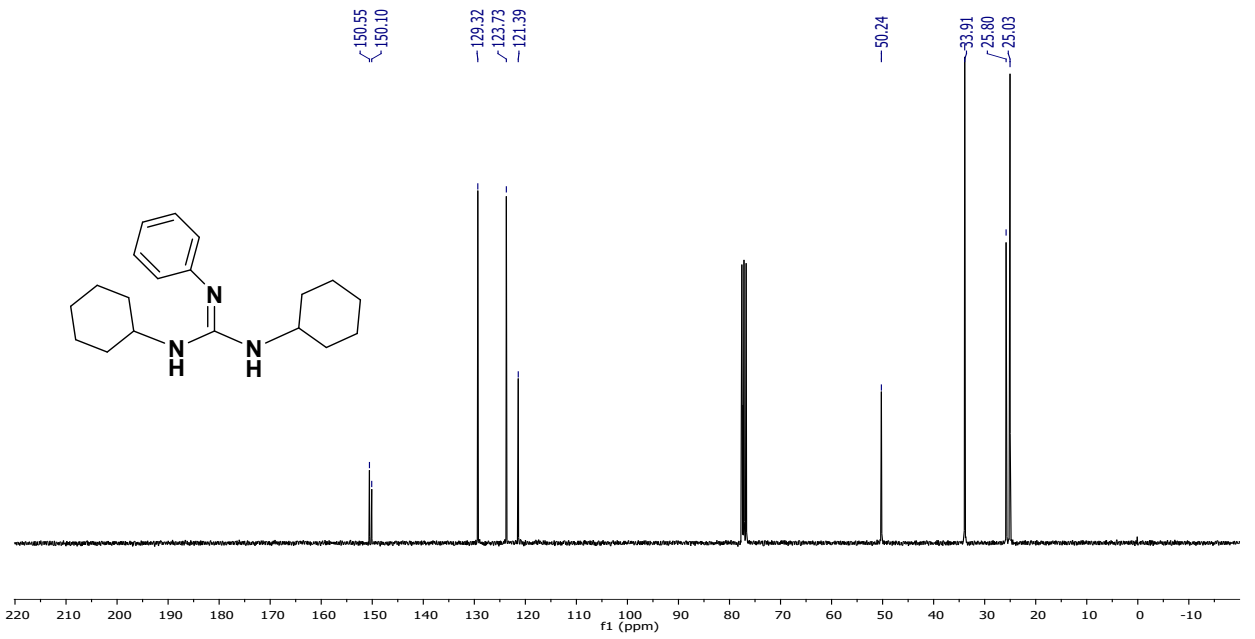


Figure FS43. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3q.**

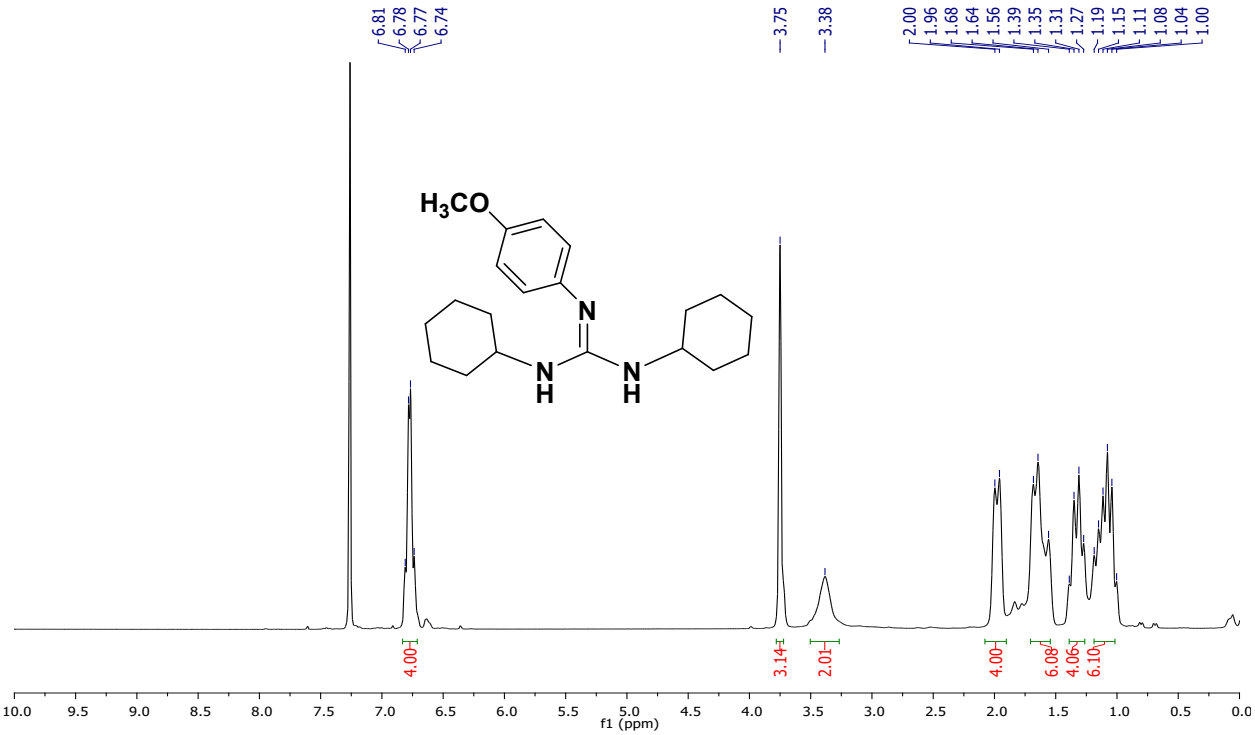


Figure FS44. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3r**.

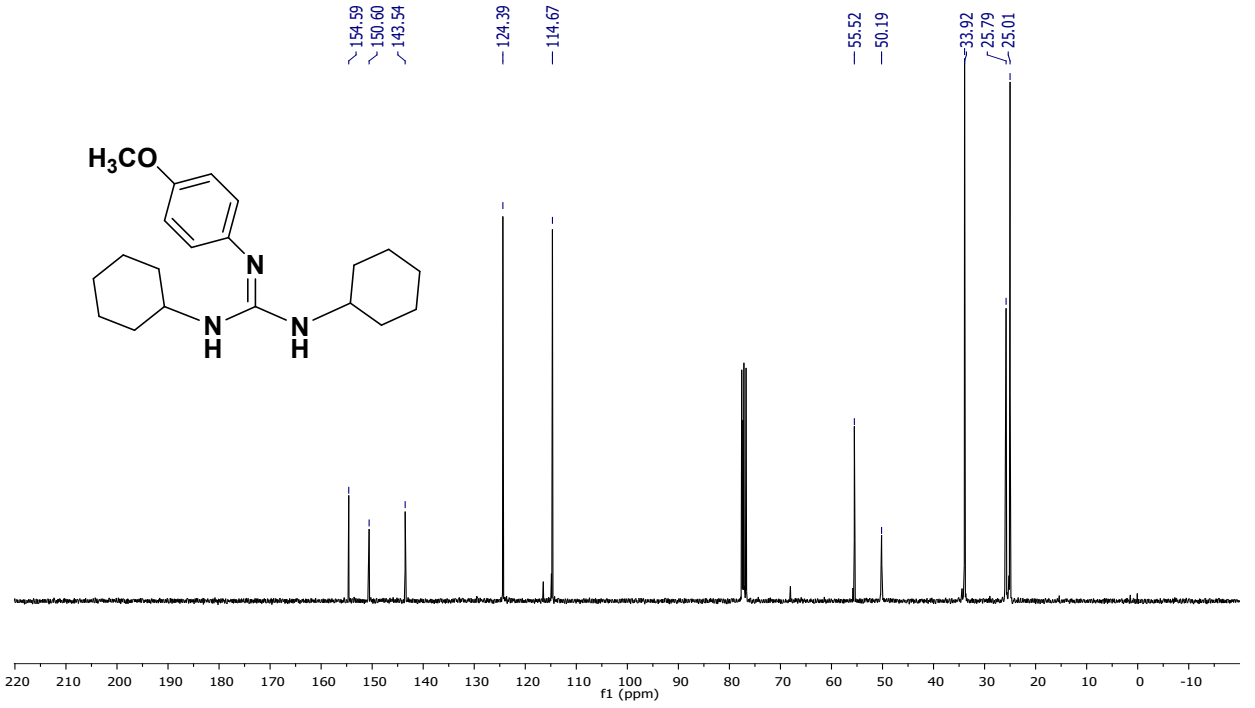


Figure FS45. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3r.**

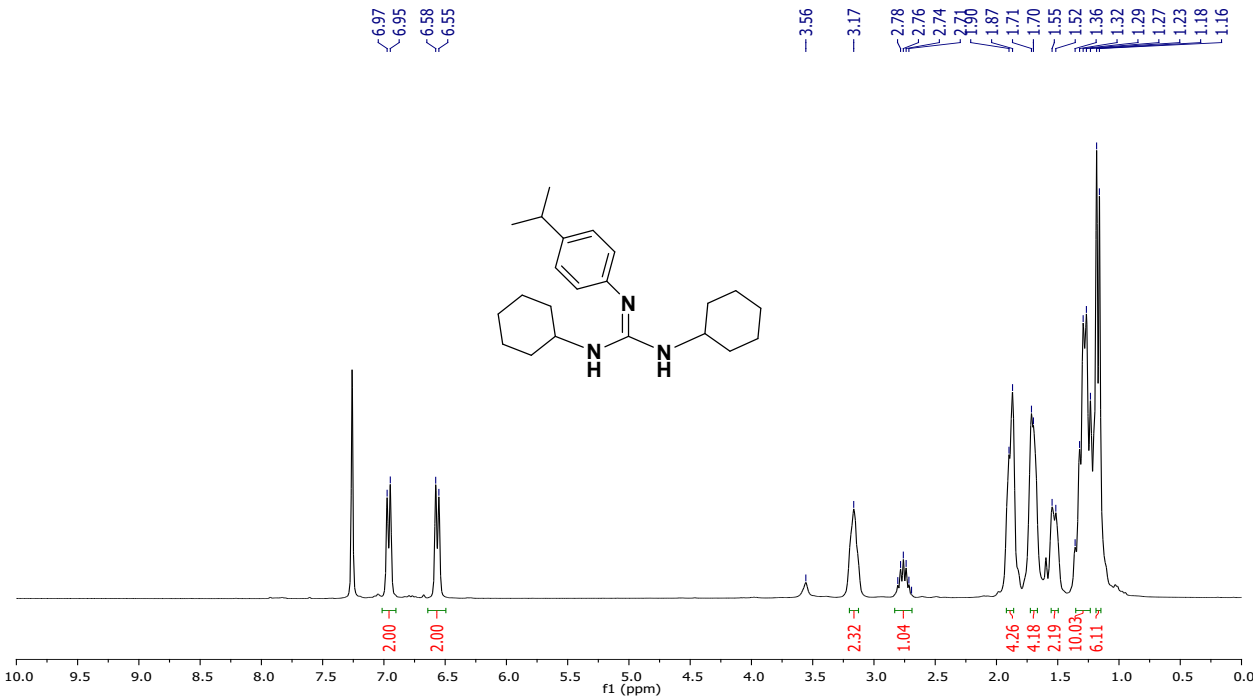


Figure FS46. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3s**.

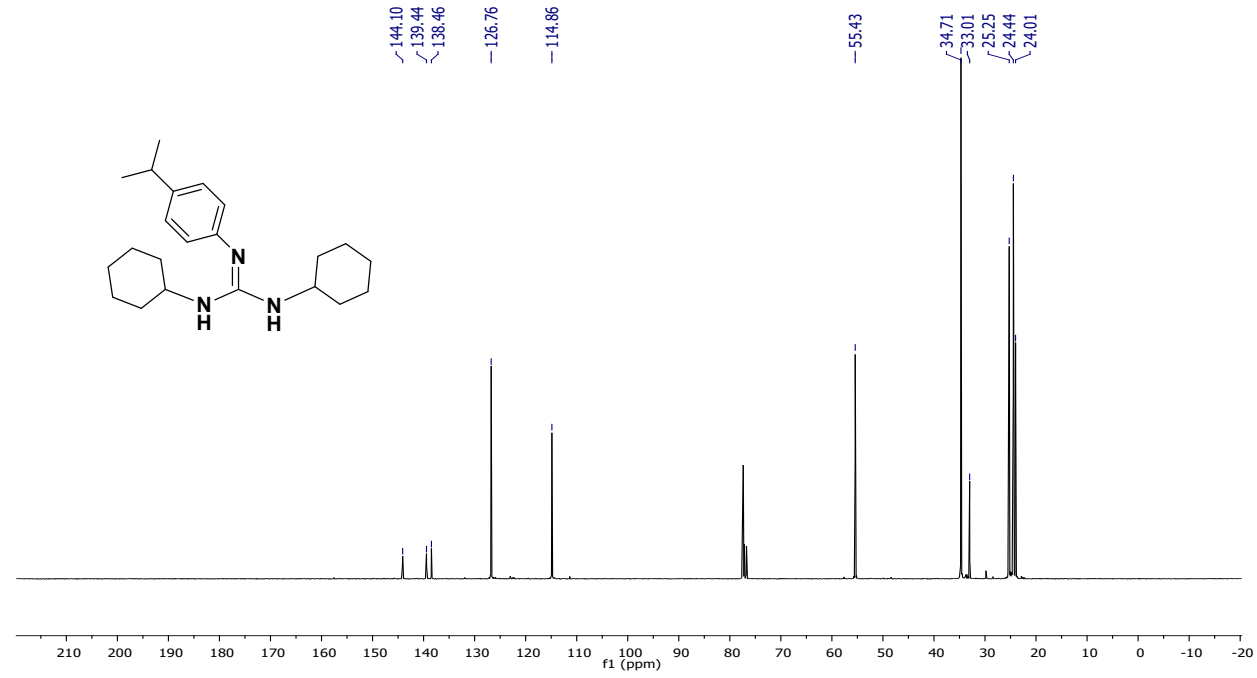


Figure FS47. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3s.**

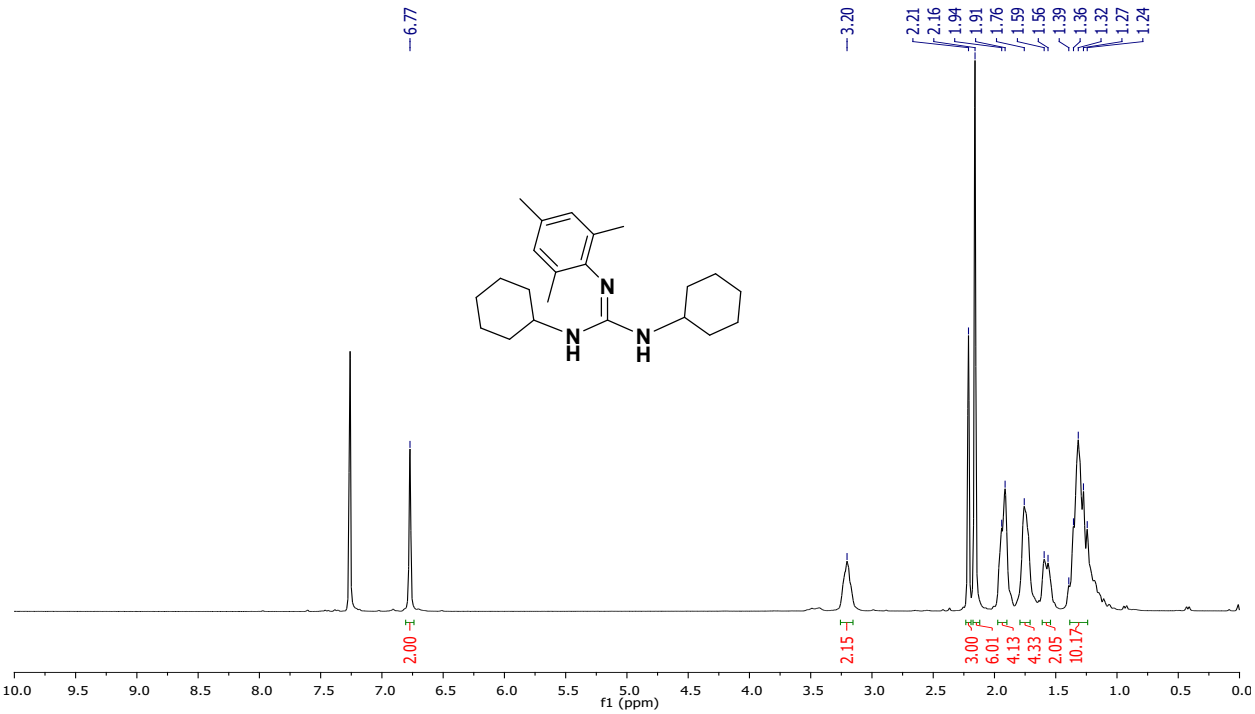


Figure FS48. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3t**.

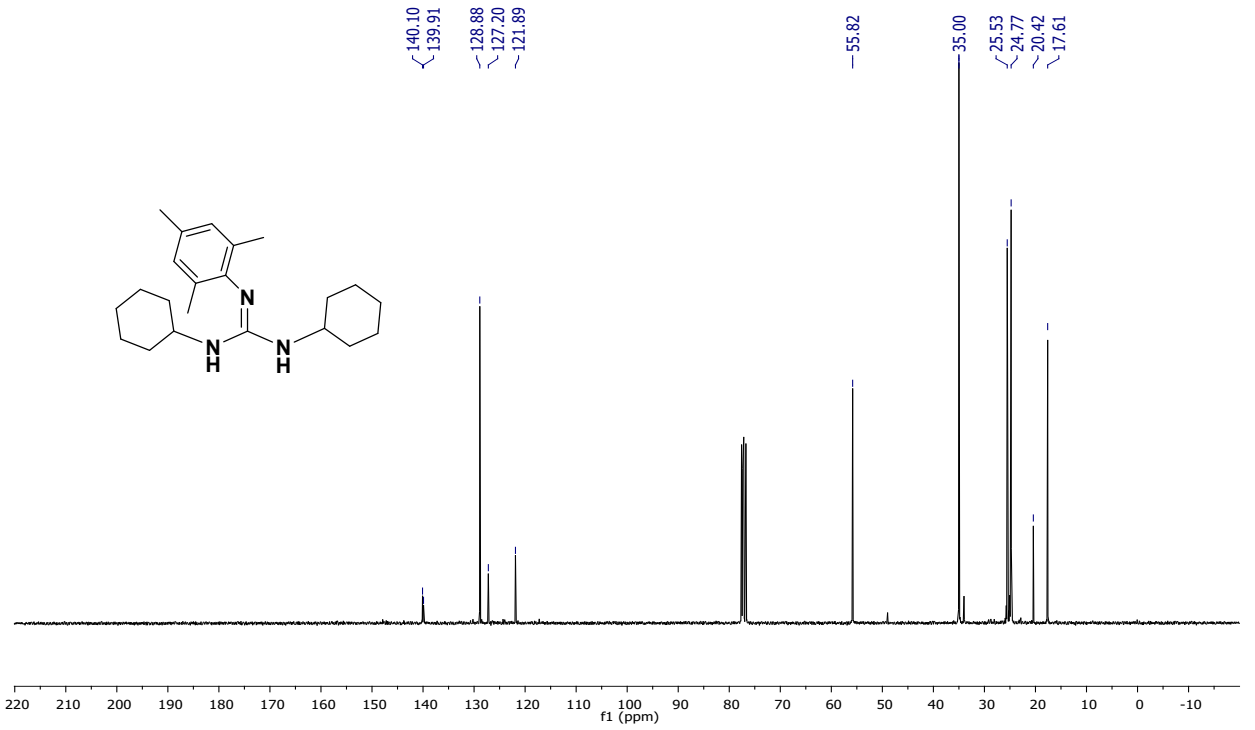


Figure FS49. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3t.**

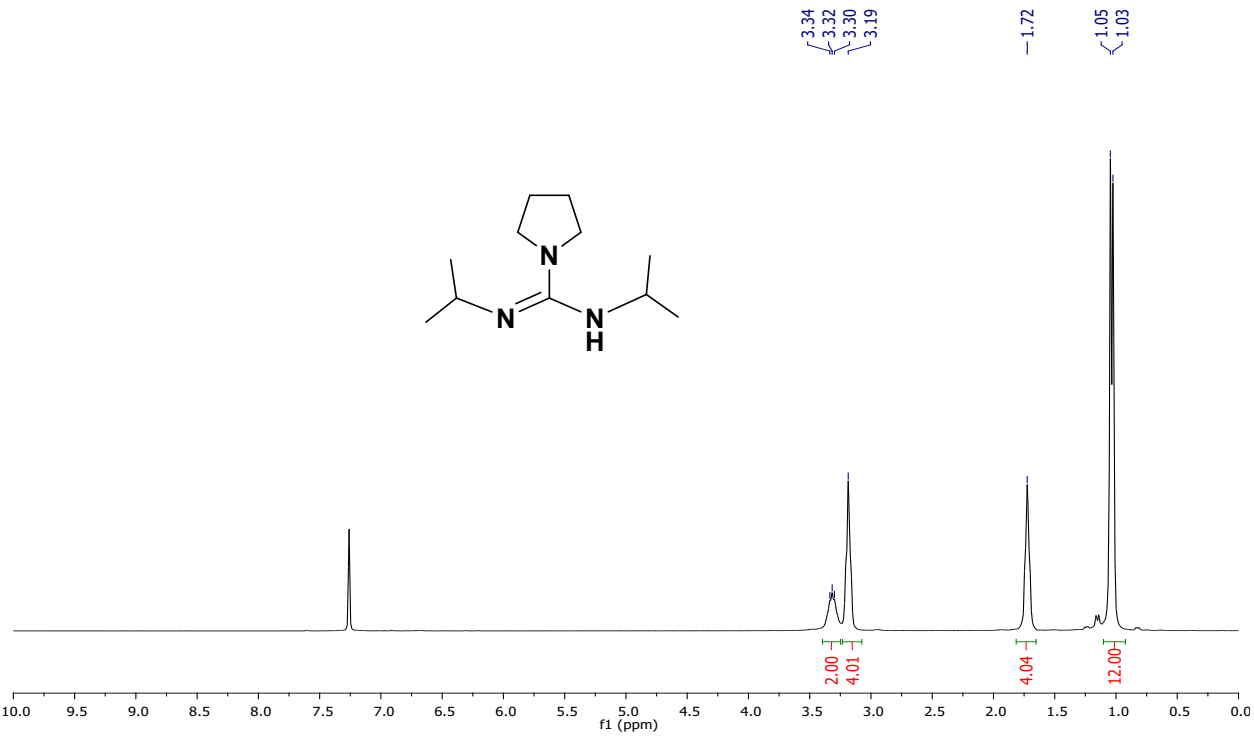


Figure FS50. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3u**.

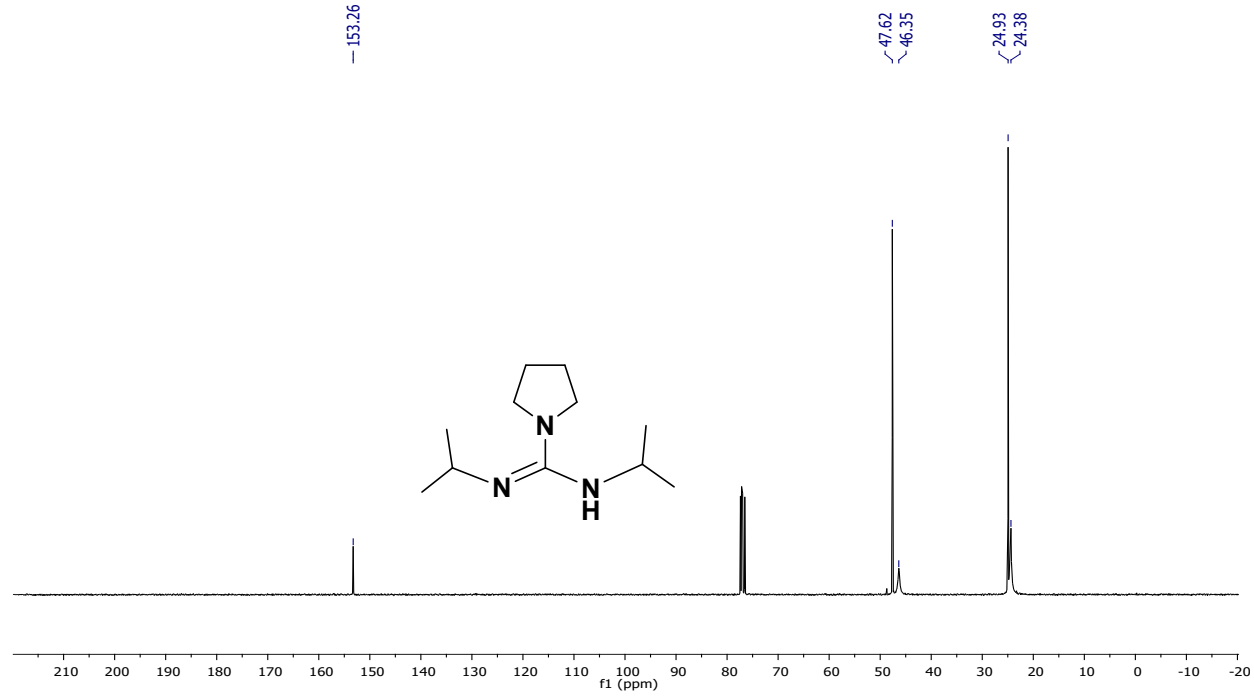


Figure FS51. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3u.**

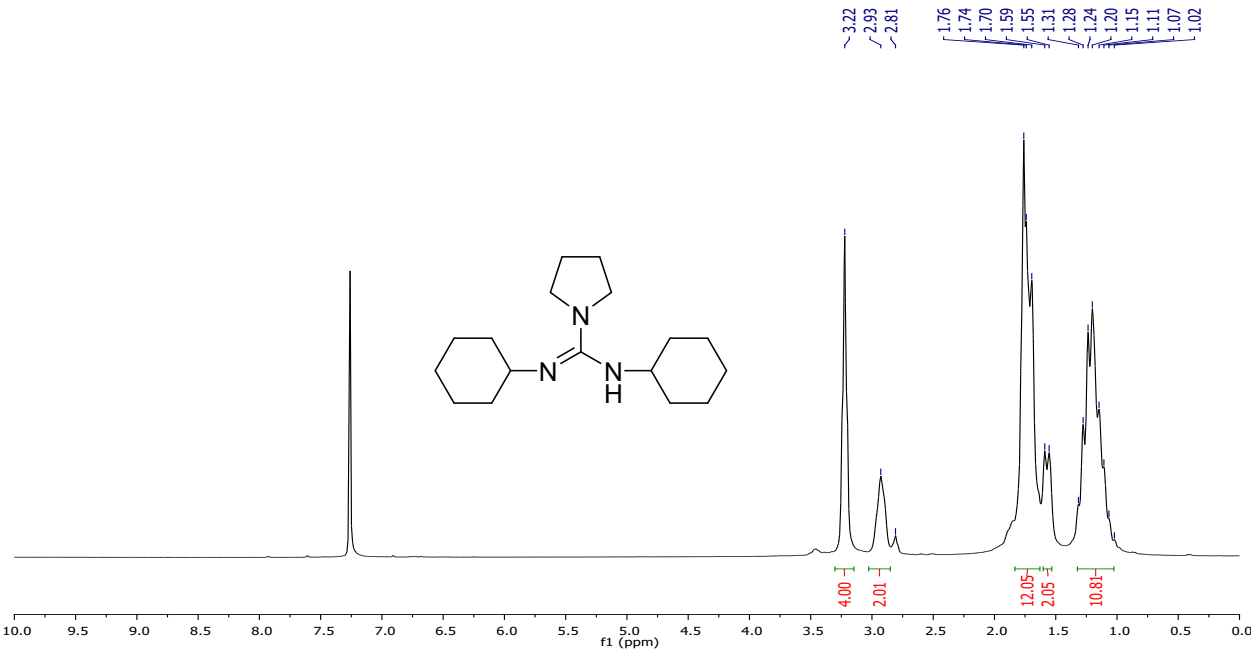


Figure FS52. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) spectrum of **3v**.

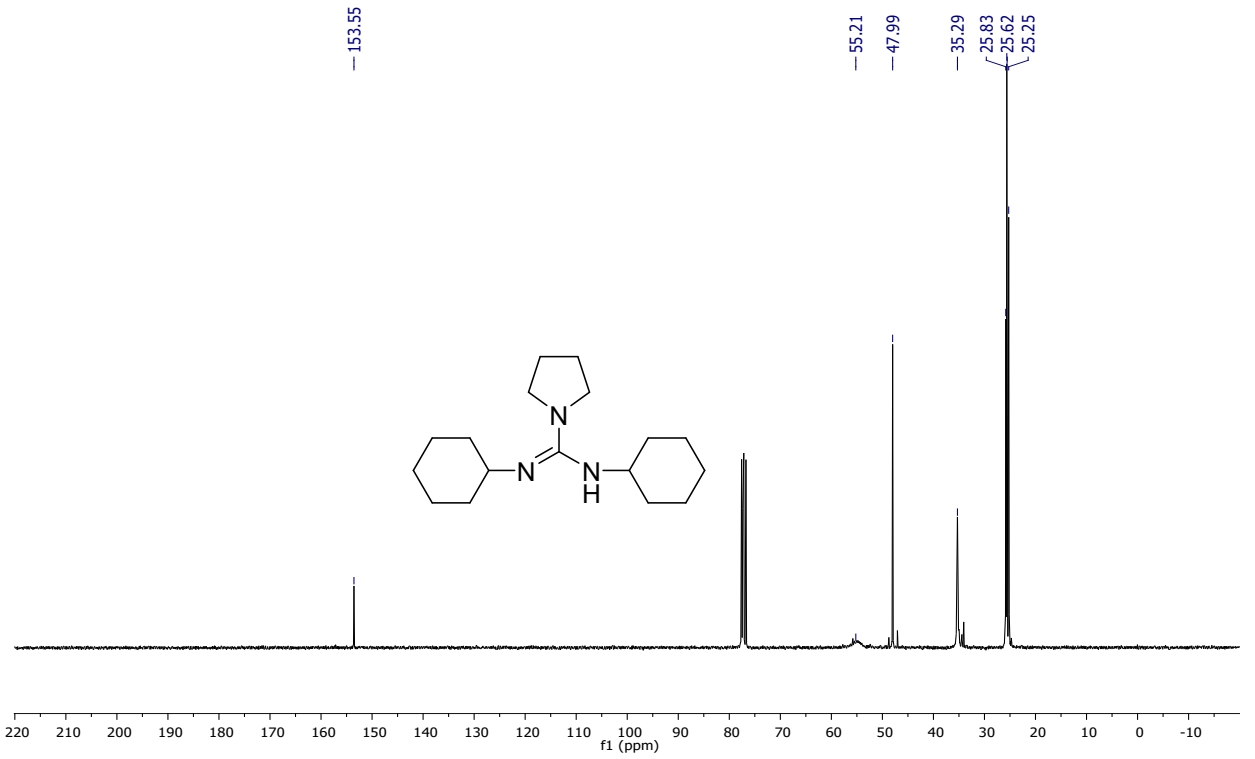


Figure FS53. $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) spectrum of **3v.**

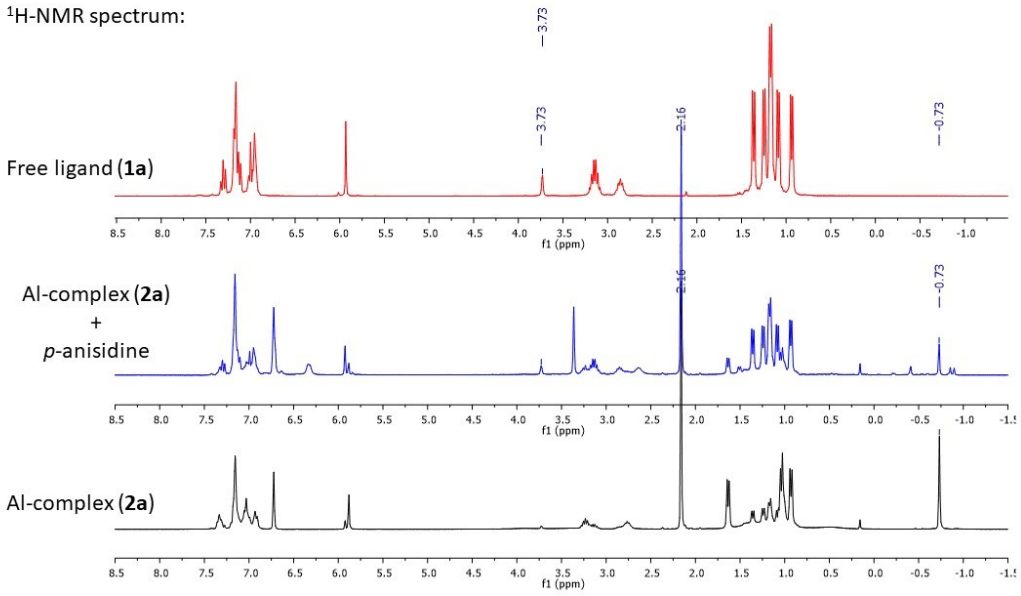


Figure FS54. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of stoichiometric reaction between complex **2a** and *p*-anisidine (1:2) after 5 h at room temperature.

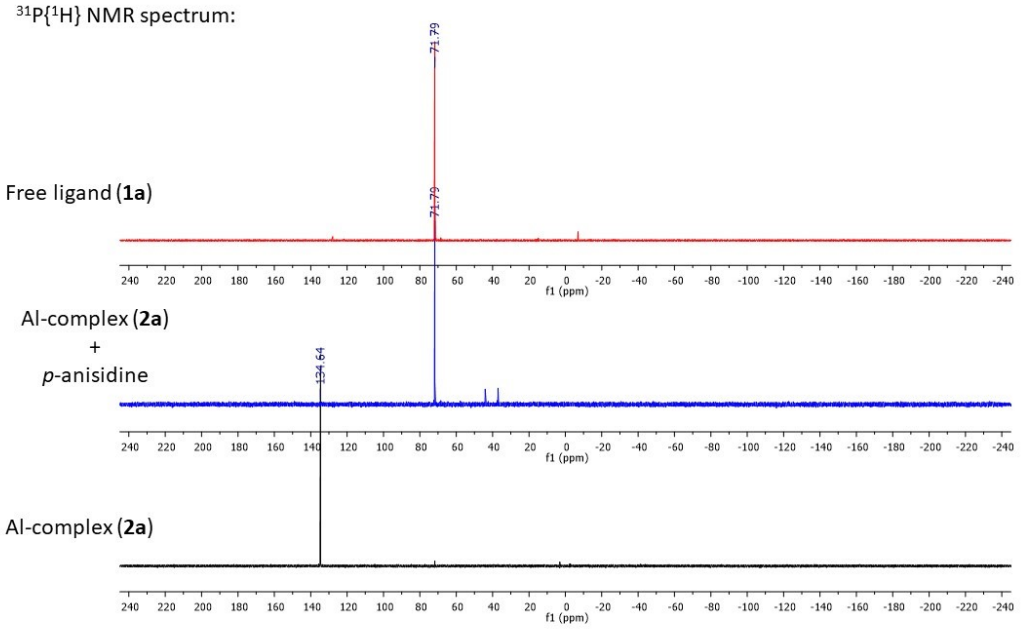


Figure FS55. ^{31}P{^{1}H} NMR (300 MHz, 25 °C, C_6D_6) spectrum of stoichiometric reaction between complex **2a** and *p*-anisidine (1:2) after 5 h at room temperature.

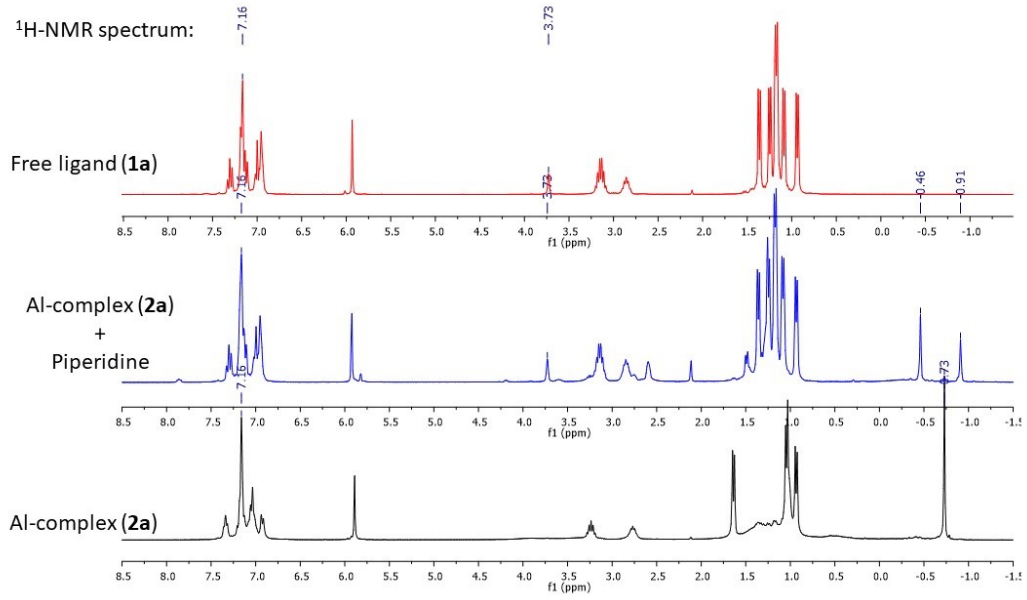


Figure FS56. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of stoichiometric reaction between complex **2a** and piperidine (1:2) after 5 h at 70 ºC.

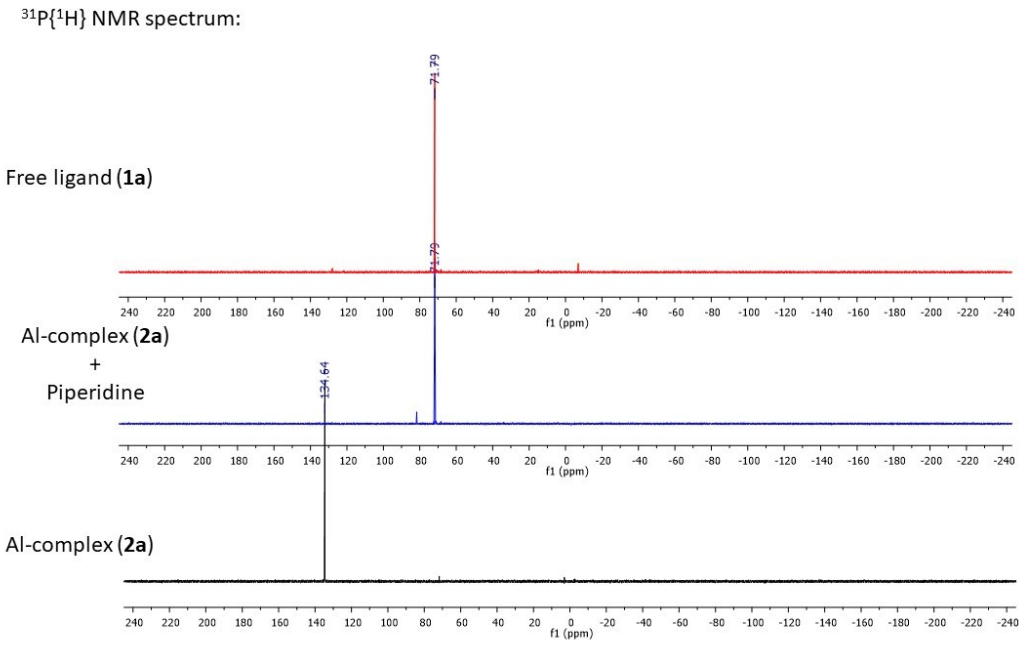


Figure FS57. ^{31}P{^{1}H} NMR (300 MHz, 25 °C, C_6D_6) spectrum of stoichiometric reaction between complex **2a** and piperidine (1:2) after 5 h at 70 ºC.

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